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# A PRELIMINARY ASSESSMENT OF THE ENVIRONMENTAL VULNERABILITY OF MACHIAS BAY, MAINE TO OIL SUPERTANKERS

by Stephen F. Moore Robert L. Dwyer and

Arthur M. Katz



Massachusetts Institute of Technology

Cambridge, Massachusetts 02139

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Page	Line	Correction	
16	6	Sketetonema should be skeletonema	
31	1	deverse should be diverse	
32	2	Lanzier should be Lauzier	
35	15	lapillas should be lapillus	
35	34	dibranchiate should be dibranchiata	
37	1	vinens should be virens	
37	31	doninat should be dominant	
43		benthos should be benthic biomass	
58	13	$.5+.8e^{.2s}$ should be $2.5e^{.2s}$	
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92	8	Castropods should be Gastropods	
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140		Full should be Fall	
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147	8	vinins should be virens	

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by Stephen F. Moore Robert L. Dwyer and Arther M. Katz

> Report No. MiTSG 73-6 Index No. 73-306-Cwm

SEA GRANT PROJECT OFFICE

# Administrative Statement

Stephen F. Moore, Robert L. Dwyer and Arthur M. Katz evaluating the biological and environmental impact of a supertanker port on the Machias Bay region of Maine, present an excellent summary of background information and the controlling factors affecting their assessment of the problem. Their summary of data on the composition and characteristics of crude petroleum and of petroleum products along with the effects of oil on marine organisms, provide an excellent general digest applicable to a wide range of related problems and situations. Their primary conclusion is that this region is highly vulnerable to oil spill hazards given the current capabilities and technology to contain and to clean up oil contamination.

The research project study and this final report have been accomplished as an element of the M.I.T. Sea Grant Program. Project support funds were provided by the Ccuncil for Environmental Quality, through a supplemental grant to M.I.T. Coherent Area Project Grant No. 2-35150 by the National Sea Grant Office, National Oceanic and Atmospheric Administration, U.S. Department of Commerce.

> Alfred H. Keil Director

January 1973

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i

# TABLE OF CONTENTS

.

				Page
1.	SUMMA	RY		1
2.	INTRO	DUCTION		3
	2,1	Objectiv	es and Scope	3
	2.2	Site Dee	cription and Study Provisions	3
	2.3		tion of the Report.	8
	2.5	organiza		
3.	A FRA	AMEWORK FO	R ASSESSING CHANGES IN ENVIRONMENTAL QUALITY	9
	3.1	_		10
	J.1	Processe	5	
		3.1.1	Inputs	10
		3.1.2	Transport and Dispersion	12
		3.1.3	Biological Transfers and Modifications	13
		3.1.4	Biological Effects	13
		3.1.5	Ultimate Fate	15
		2.1.2		
	3.2	Basic Pr	inciples of Ecology	15
		3.2.1	Organizational Principles	15
		3.2.2	Dynamics	19
		<i>J.2.2</i>		
	3.3		ion Needs and Synthesis for Assessing Environ-	
		mental V	ulnerability	23
		3.3.1	Definition of Existing Conditions	26
		3.3.2	Definition of Proposed Environmental Changes	28
		3.3.3	Determination of Specific Biologic Responses	28
4.	DESCI	RIPTION OF	EXISTING CONDITIONS - THE EASTERN COAST OF MAINE	30
	4.1	Physical	Description	30
		( 1 1	Coastal Physiography	30
		4.1.1		31
		4.1.2	Coastal Hydrography and Climate	34
		4.1.3	The Machias Bay Region	74
	4.2	Biologic	al Description of the Coastal Waters of Maine	34
		4.2.1	Intertidal Communities	34
		4.2.2	Subtidal and Pelagic Communities	41
5.	COMPOSITION AND CHARACTERISTICS OF CRUDE PETROLEUM AND PETROLEUM			
				44
	1 100			
	5.1		tion	44
	5.2	An Introd	luction to Organic Chemistry	44

				Page
	5.3	Composit	ion of Petroleum	49
		5.3.1	Hydrocarbons	49
		5.3.2	Non-Hydrocarbons	52
		5.3.3	Classification by Boiling Point Distribution	52
	5.4		hering	53
				÷-
6.	EFFEC	TS OF OIL	ON MARINE ORGANISMS	63
	6.1	Introduc	tion	63
		6.1.1	A Framework	63
			6.1.1.1 Individuals	63
			6.1.1.2 Higher Levels of Organization	66
			official adjoint of organization	00
		6.1.2	Data Base	69
	6.2	Effects	of Oil on Individuals	72
		6.2.1	Lethal Toxicity	73
			6.2.1.1 Flora	73
				74
			6.2.1.3 Benthic Fauna	75
			6.2.1.4 Summary of Toxicity Data	91
		<		0.7
		6.2.2	Sub-lethal Effects on Behavior	91 07
		6.2.3	Incorporation of Hydrocarbons	96
			6.2.3.1 Cancer and Polycyclic Aromatic Hydro-	
			carbon Compounds	97
			6.2.3.2 Tainting	102
		6.2.4	Coating	104
		6.2.5	Habitat Changes Caused by Spilled Oil	109
	6.3	Summary		110
7.	POTEN	TIAL SPIL	L TRAJECTORIES AND BEHAVIOR	113
	7.1	Introduc	tion	113
	7.2	Basic Mo	del	113
		7.2.1	Mechanics Governing Spreading	113
		7.2.2	Trajectory of a Spill	119
				-
	7.3	Data Bas	e	121
		7.3.1	Currents	121
		7.3.1		122
		* • • • • •		
	7.4	Cdma-1-44	on Toobalaus	125
	1.4	STURIALI	on Technique	

~

		D	_
	7.5	Pag Catastrophic Spills	5
	7.6	Chronic Spills	
8.	ASSES	SMENT OF ENVIRONMENTAL VULNERABILITY	
	8.1	Introduction	
	8.2	Oil Spill Events	
		8.2.1 Catastrophic Spills	
		8.2.1.1 A 30,000 Ton Spill	
		8.2.2 Chronic Spills	
	8.3	Non-Oil Spill Events	
	8.4	Summary	
9.	CONCL	USIONS AND RECOMMENDATIONS	
10.	REFER	ENCES	

#### 1. SUMMARY

The objectives of this report are to assess as clearly as possible the environmental vulnerability of Machias Bay, Maine, to oil supertankers. The biological effects of chronic and catastrophic oil spills and non-oil spill events are considered. Environmental vulnerability as used herein expresses both the magnitude and probability of biological changes resulting from specified events. The impacts of these events are evaluated for several levels of biological organization: individuals, populations, communities and ecosystems.

In order to understand the effects of oil on marine organisms it is necessary to recognize the complex chemical characteristics of oil. Hydrocarbons are the primary constituents of oil, and are divided into eight fractions according to hydrocarbon type (paraffin, cyclo-paraffin, aromatic and naphtheno-aromatic) and boiling point. This characterization provides sufficient flexibility for describing biological effects of oil and the physical/chemical dynamics of spilled oil, especially oil weathering.

The effects of oil on individual organisms are classified as: 1) lethal toxicity; 2) sub-lethal disruption of cellular level processes causing disruption of behavioral patterns; 3) incorporation of hydrocarbons in organism tissue; 4) lethal and sub-lethal effects of coating of organisms with oil, which mechanically interferes with organism activities; and 5) alterations in habitats caused by deposition of oil on substrates such as rocks, sand and mud. A review of literature indicates that significant sub-lethal effects may result from concentrations of water soluble aromatic hydrocarbons as low as 10-100 ppb. Lethal toxicity may result from water soluble

aromatic concentrations of .1-1 ppm for most larval stages and 1-100 ppm for most adult organisms. The ultimate effects of an oil spill to populations, communities and ecosystems is not as well understood. However, most marine populations have evolved reproductive strategies which provide a high probability of population survival in the face of major environmental disturbances. Therefore, eventual recovery of higher levels of biological organization from single events is very likely. Permanent changes in biological systems are most likely to occur where repeated spillage of oil takes place.

The assessment of environmental vulnerability requires estimation of location and trajectories of hypothetical oil spills. A simple model of slick transport by wind induced currents indicates that there is a relatively high probability (10-50%) that 10-20 miles of shoreline would be covered by a major oil spill. The results depend upon spill size, point of release, season of the year, and offshore current assumptions. Tidal currents are not included in the model because of lack of data and the complexity of the model needed for such a description.

It is concluded from these considerations that Machias Bay is highly vulnerable environmentally to oil supertankers. The release of a major catastrophic spill (30,000 tons) is expected to occur as frequently as once in twenty years and a moderate spill (500 tons) once every year. The biological effects of these are likely to be very extensive with some localized permanent changes in communities. Chronic spills and non-oil spill events are not likely to cause major biological problems.

#### 2.1 Objectives and Scope

The objective of this report is to establish as clearly as possible the environmental vulnerability<sup>1</sup> of Machias Bay, Maine to a proposed oil supertanker terminal. The environmental vulnerability assessment focuses on the biological consequences of hypothetical events relating to the construction and operation of such a terminal. The results of this study are based on the current "state-of-the-art" with regard to our understanding of the biological response to environmental changes of interest and the ability to predict the actual consequences of such events for the Machias Bay region. In this context, the study is a review and interpretation of literature. No primary data collection has been undertaken. This report does not consider impacts of activities resulting from the terminal installations such as industrial development, air pollution, urbanization, etc. In section 3 a possible framework is proposed for assessing impacts of environmental changes which has more general application than the specific problems discussed herein.

# 2.2 Site Description and Study Provisions

The general location of Machias Bay, Maine is illustrated in Figure 2-1. Machias Bay, the approach to Machias River and the towns of Machiasport and Machias, is a typical rocky, northern New England embayment. The bay is about six miles long and one to three miles wide. Libby Islands is the principal guide to the entrance of Machias Bay (see Figure 2-2). The general study area is the coastal region bounded by 67° longitude on the east and 68° longitude on the west. Coast and Geodetic Survey Nautical Charts Numbers 1201 and 304 provide a basic source of information on the geography of this area.

<sup>&</sup>lt;sup>1</sup>Vulnerability and related concepts as used in this report are defined and discussed in sections 3.3 and 8.

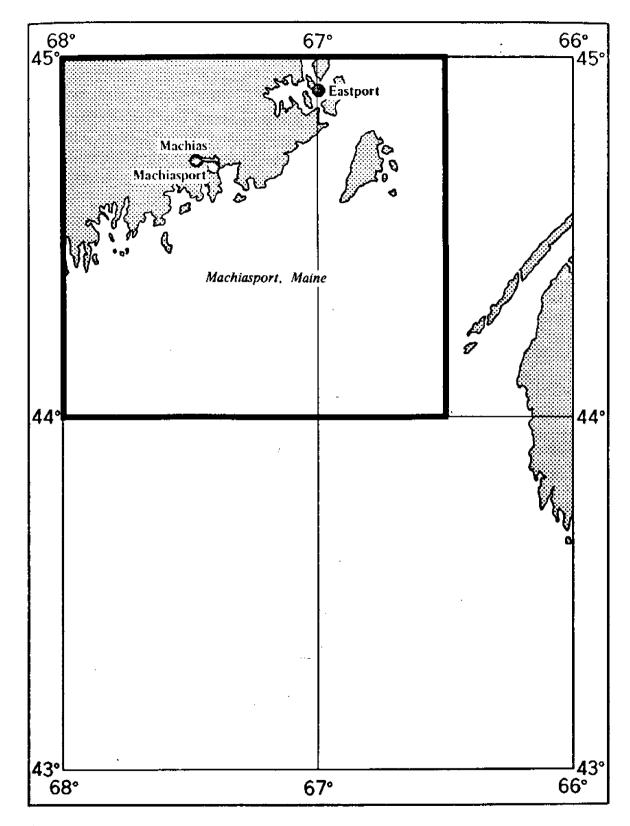


Figure 2-1. Machias Bay, Maine, Area Location Map (from Brower, et al., 1972)

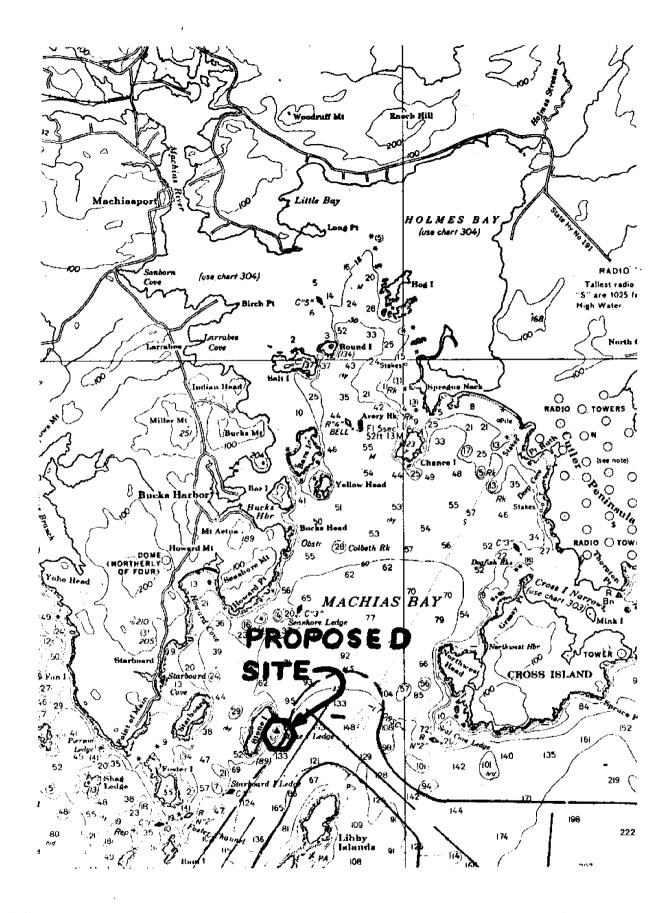


Figure 2-2. Machias Bay, Maine, showing proposed supertanker terminal site (Coast & Geodetic Survey, Nautical Chart No. 1201)

The proposed terminal facility would be located on the eastern side of Stone Island (Figure 2-2). Jetties off the island into one-hundred foot deep water would be constructed to provide adequate protection of the berthing facility. In addition a 650 yard breakwater running northeast from Libby Island and a 1,300 yard breakwater running south of Seal Cove Ledge from Cross Island will be required. The berthing facility itself would be a dolphin-and-rack type approximately 1800 feet long. Transshipment to shore would be by small tankship or pipeline.

Two types of oil spills are considered in this study: 1) periodic (chronic) spillage occurring during transshipment operations; and 2) catastrophic spillage due to a major tanker collision. Periodic spills are assumed to occur at the berthing facility. The major catastrophic spill is assumed to occur somewhere in the approach channel (several possibilities are considered).

The frequency and amount of spillage has been provided as a basic input to this study (Jellinek, personal communication). These data are as follows:

#### PERIODIC SPILLAGE

1. Year: 1980

Amount: 555 Bbls.

Frequency: 1.5 Bbls/day or 30 gals/supertanker operation and 4.8 gals/transshipment operation. (391 supertankers per year and 2,445 transshipment operations per year).

Location: at the berth

Year: 2000
 Amount: 1,150 Bb1s.

Frequency: 3.2 Bbls/day or 30 gals/supertanker operation

(802 operations) and 6 gals/transshipment

operation (4,011 operations).

Location: at the berth.

#### CATASTROPHIC SPILLAGE

Release Time: 2 hours

Size: #1: 500 tons

#2: 30,000 tons

Frequency: Consider the immediate and cumulative effects of a 500 ton spill yearly for twenty years and one 30,000 ton spill mid-way through the twenty year period.

Location: See Figures 7-4a and b

Two different types of crude oils are assumed, representative of African or Middle Eastern oils. The characteristics and composition are given in Table 2-1.

	A	В
Sulfur, percent	0.14	1.30
Nitrogen, percent	0.083	0.042
Color	brown-black	brown-black
Specific gravity	0.858	0.840
API gravity	33.4	37.0
Light gasoline	2.4	7.3
Total gasoline and naptha	15.1	30.3
Kerosene distillate	13.1	9.9
Gas oil	10.3	15.2
Nonviscous lubricating distillate .	14.8	11.3
Medium lubricating distillate	4.3	6.8
Viscous lubricating distillate	~~	3.5
Residuum	42.2	19.4
Distillation loss	0.2	3.6
3, 4 benzpyrene*	1320 µg/kg crude	400 µg/kg crude

Table 2-1: Crude Oil Characteristics.

Crudes A and B would also contain compounds such as 1,2 benzanthracene, 1,2 - benzphenanthrene, diphenylmethane, phenanthrene, and dibenzthiophene in the general proportions indicated by the benzpyrene content of each. In addition to the impacts of oil spills this study also considers the non-spill effects of terminal construction and existence and tanker operation. The emphasis, however, is on the oil spill effects. Due to the physical characteristics of the Machias Bay site, non-spill impacts are relatively small (a primary reason for its selection as a potential site).

#### 2.3 Organization of the Report

The remainder of the report is divided into eight sections. In Section 3 a basic framework for assessing impacts of environmental changes in suggested. This section outlines the information needs and major uncertainties dealt with in subsequent sections. Section 4 describes the existing conditions in the study area, in so far as they can be estimated. There is little definitive data, both biological and hydrographical describing the Machias Bay region. In Section 5 the characteristics and composition of petroleum substances are discussed. This background information is essential for understanding the interpretations presented in Section 6 of the biological effects of oil on marine organisms. The possible spill trajectories are considered in Section 7 and the actual assessment of environmental vulnerability made in Section 8. Sections 9 and 10 are, respectively, Conclusions and References.

# 3. A FRAMEWORK FOR ASSESSING CHANGES IN ENVIRONMENTAL QUALITY

Living organisms must continually cope with fluctuations in the environment. Variations may be relatively short-term such as day-to-day or seasonal changes in temperature and salinity, or long-term such as evolutionary differences between lakes and oceans. The sum total of short-term adaptations leads to the process of natural selection - "survival of the fittest".

Different animals successful in producing offspring and therefore maintaining their species have different ways of handling changes in the environment. These may be classified as physiological, behavioral and morphological. Physiological changes refer to internal adjustments by the organism to cope with a change in the environment. For example, fish control their internal salinity as the external water salinity changes. Behavioral changes are commonly accompanied by physiological changes. The relationship between physiology and behavior, or even behavior itself, in many animals is not well understood. A typical example of a behavioral change is the vertical movement in the ocean of many small marine animals called copepods. These organisms respond to light and temperature changes which govern their feeding behavior. Also, of course, organisms that are mobile can simply escape undesirable environmental conditions by moving to a more satisfactory area.

These mechanisms of adaptation only work within certain ranges of environmental change. Some shifts in the environment may be so large or happen so quickly that even the built-in adjustment mechanisms of the organism are not capable of successfully compensating for the stress caused by the change. In general, the animals that have evolved to survive in a particular environment have the ability to successfully adapt to the range

of environmental variations which occur naturally. However, even these "historical stresses" are occasionally exceeded and individual animals succumb. For example, a storm such as Hurricane Agnes can result in such high influxes of fresh water into embayments and estuaries that shellfish such as oysters and clams cannot survive the resulting reduction in salinity.

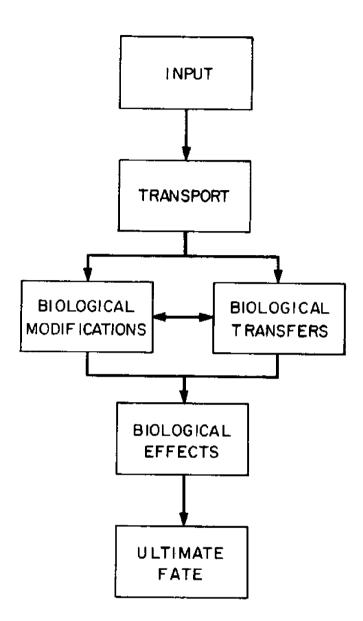
Animals must also cope with man-made changes in the environment. Some of man's activities, such as discharging heated water from power plants, expose organisms to changes which are "historical". However, in other cases, as far as is known, the organisms have not been subject to the environmental change imposed. In the latter situation organisms may not have evolved any adaptation mechanism for surviving under such "artificial" stresses. In either case, animals have some range of tolerance, although possibly very small, over which they can successfully respond and maintain a normal life pattern. With respect to man-made environmental changes, the question becomes not, will there be a change in the biological systems, but rather, what is the intensity, nature and implications of the change. The following sections attempt to provide a framework for evaluating the effects of such changes.

#### 3.1 Processes

Figure 3-1 illustrates five basic processes which contribute to the impact of environmental changes, resulting from the discharge of foreign substances into the environment.

#### 3.1.1 Inputs

The ultimate impact of any chemical introduced into the environment depends upon the amount, location and temporal distribution of the input, as well as the chemical form and state of the substance. A small amount of a highly concentrated substance can be more damaging than a large total input



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FIGURE 3-1 BASIC PHYSICAL AND BIOLOGICAL PROCESSES CONTRIBUTING TO ENVIRONMENTAL IMPACTS

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of the same chemical distributed over a large area and long enough period of time, so that toxic concentrations never develop. However, low concentrations of some chemicals maintained over long time periods (say, years) may result in greater long-term damage, due to interference with important behavior patterns rather than direct toxic poisoning.

In addition, the chemical characteristics of any materials are also important. Large, complex molecules called polycyclic aromatic hydrocarbond (PAH) appear to be widely distributed in the environment (Zobell, 1971). Most of these substances are inactive, however, a few, which have only slight structural modifications, are potent carcinogens.

Knowledge of these input characteristics are necessary to evaluate effects on the organisms and on the quality of the environment. Such knowledge is often difficult to obtain and estimates are based on sparse, incomplete data and unverifiable assumptions.

3.1.2 Transport and Dispersion

The transport and distribution of materials in the (marine) environment depends upon physical, chemical and bio-chemical processes. The physical processes of interest are the mass movements of the medium in which the chemical is carried: water, air, sediments, and/or organisms. Evaluation of transport processes requires information about the movement of the medium and the concentration of the substance in the medium. Also, it is necessary to know the chemical form of the substance. For example, the effects on the environment often depend on whether material transported in water is dissolved or in particulate form.

Chemical and bio-chemical reactions often occur within the transport medium. Therefore, the chemical originally introduced into the environment may undergo important changes. Some of the components of oil are highly volatile and a spreading slick changes chemical characteristics markedly.

Other substances are ingested by organisms in one place and transported to another area by the organism. The chemical characteristics of the material may or may not be altered by metabolism.

The complexity of these transport processes makes accurate prediction very difficult. Many of the physical processes are reasonably well-known. However, biologically mediated transports have not been studied for most substances.

3.1.3 Biological Transfers and Modifications

The important processes which contribute to biological transfers and modifications are illustrated in Figure 3-2. These processes may profoundly alter the substance of interest by either modifying the chemical nature of the material in bio-transformations (metabolism) or accumulating the substance by tissue storage to concentrations far in excess of that normally encountered. Substances which are not excreted immediately become distributed throughout the food web. One organism feeding on another and that one on another and so on, results in the movement of stored substances from one organism to the next, usually increasing the concentration in the process.

3.1.4 Biological Effects

Biological effects of materials on organisms are distinguished from biological transfers and modifications which deal with biological effects <u>on</u> the substances. The specific biological effects of oil are dealt with in detail in Section 6 of this report. The detail of the effects are better understood after basic ecologic principles have been discussed (Section 3.2). Suffice it to say at this point that while specific actions of a pollutant occur on individual organisms, the effects are cascaded throughout the environment by the resulting changes in populations and communities of organisms. The greatest levels of uncertainty are in these cascading effects.

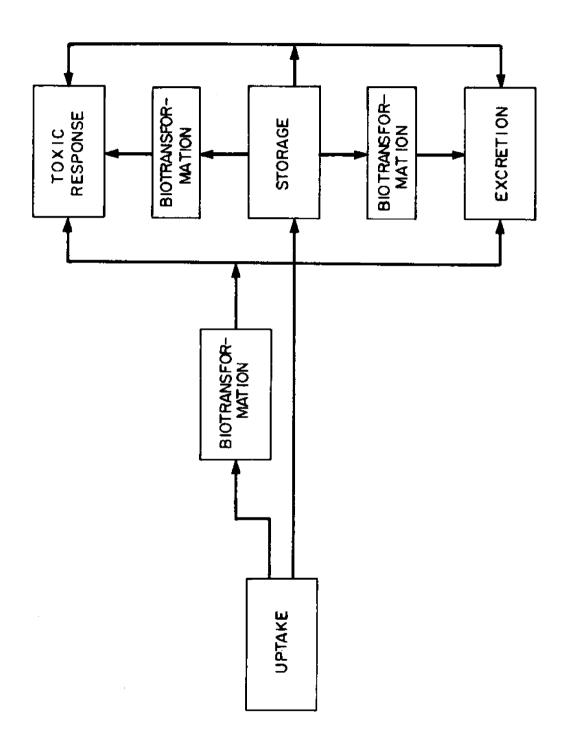


FIGURE 3-2 BIOLOGICAL TRANSFERS AND MODIFICATIONS THAT MAY EFFECT IMPACT OF SUBSTANCES DISCHARGED INTO THE ENVIRONMENT

#### 3.1.5 Ultimate Fate

Some materials introduced into the environment may cycle through the environment endlessly; some, may be incorporated in sediments and essentially removed from biological considerations; others are degraded to stable innocuous materials such as CO<sub>2</sub>. The ultimate fate depends on whether the material is, in fact, degradable or not. Non-biodegradable substances pose the most serious threats to the environment.

# 3.2 Basic Principles of Ecology

This section is provided to introduce the reader to the basic principles of ecology. Because of the variability of terminology prevalent in ecology, the reader familiar with ecologic principles is advised to review the material presented here. In this way, confusion due to definitions can be avoided.

Ecology is the study of the relationship between organisms and their environment. Therefore, it is the branch of biology which can be expected to provide a basis for assessing impacts of environmental changes. The text by Odum (1971) is an excellent detailed development of the fundamental principles of ecology. The subject material presented below is divided into parts: organizational principles and dynamics.

3.2.1 Organizational Principles

The biological world may be subdivided in many different ways. A convenient arrangement for our purposes is to consider five levels of organization: cell, organism, population, community and ecosystem. A <u>cell</u>, which is a complex collection of specialized molecules, is the basic living biological unit. Some single cells are complete organisms in themselves and are called microbes. Examples are bacteria and most algae. Higher level

organisms such as marine invertebrates are assemblages of specialized organs, which are in turn collections of cells. A <u>population</u> is a group of individuals of any one kind of organism. Theoretically, a population should refer to a particular species. However, the term is also commonly used more loosely to refer to the collection of individuals of similar species. <u>Sketetonema costatum</u> is a particular diatom species commonly found in the Gulf of Maine. We may be interested in the population of <u>S. costatum</u> in the Gulf of Maine waters, but we often also refer to the algal "population", which is the collection of all phytoplankton, including <u>S. costatum</u>. A <u>community</u> in the ecologic sense includes all of the populations occupying a given area. The <u>pelagic</u> community is all of the populations that live in the open water of the ocean. The community and the non-living environment function together as an ecosystem.

The designation of levels or organization is convenient, but somewhat artificial. Each level is strongly interrelated with the next and sharp lines of distinction are artificial. For example, the individual is as dependent on the population, as it is on the organs which function together to make the organism. To understand the possible impacts of changes in the environment, effects at each level and interactions between levels of organization must be analyzed.

The complex organization of biological systems is maintained by a flow of energy. The ultimate source of energy is the sun. The light energy falling on an area is converted to chemical energy by plants in the process of photosynthesis. The unicellular plants or algae which float near the water surface, are the most important "primary producers" in the marine environment. Animals (including bacteria and other microscopic organisms) obtain energy from the chemical energy stored in complex organic molecules. <u>Herbivores are animals which eat plants and use the chemical energy stored</u>

by plants in photosynthesis. Animals which eat other animals using the chemical energy stored in tissues are called <u>carnivores</u>. In the transfer of energy from one level to the next, most of the energy is lost as heat. As a result the so-called trophic (nutritional pattern) pyramid is limited to a maximum of four or five levels. The concepts of "trophic structure" are illustrated in Figure 3-3. Also, shown in Figure 3-3 is the flow of energy due to the breakdown of waste material or detritus by microorganisms. The flow of energy due to feeding patterns can be evaluated in more detail for any particular group of organisms. This type of analysis gives rise to the food web, which is usually shown as a diagram similar to those in Figure 3-4.

The flow of energy not only leads to organization of biological systems but also maintains that organization by three fundamental ecosystem processes: materials cycling, communications, and adaptations (control). The hydrologic cycle, phosphorous cycle, and nitrogen cycle are common examples of material cycles. Organisms require a variety of material resources to construct cell tissue. The cell material eventually becomes waste material and is broken down by micro-organisms, releasing the basic substances, which can be used once again in the cycle. Note that energy flow is unidirectional, but material flow is cyclic.

Communication between individual organisms and organisms and their environment is essential to the organization of biological systems. Organisms must be able to communicate for reproductive purposes certainly. But many organisms have found that organization for feeding and other behaviors is advantageous. In addition, it is necessary for an individual to be able to detect environmental changes and adjust accordingly. Feedback regulation or homeostasis is a hallmark of ecological systems.

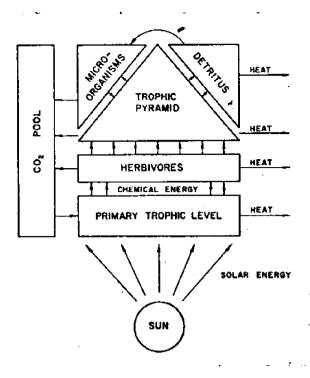


Figure 3-3. Representation of ecology in terms of energy flux indicating that ecological processes are driven by the flow of energy from the sun to thermal sinks (Morowitz, 1968).

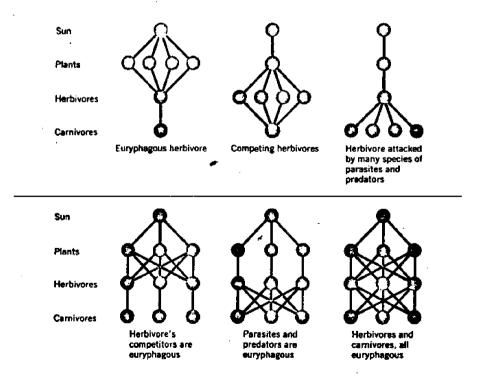


Figure 3-4. Various patterns of three-level trophic-web organization. Each dot represents a species, and lines between dots indicate that the species in the lower level eats the species on the level above. (Watt, 1968)

The goal of life is to survive and in evolutionary time innumerable strategies for survival have evolved. That is, organisms that have developed successful adaptations to their environment continue to "win the game". Adaptations may be physiological, behavioral or morphological. The process of natural selection operates to allow these organisms which are best equipped to cope with their environment. However, this process is passive, i.e. selection is by default. Regulatory mechanisms are successful adaptations to actively cope with short-term environmental changes.

## 3.2.2 Dynamics

The foregoing description has focused on a static description of structural and functional characteristics of ecosystems. However, biological systems are inherently dynamic and it is necessary to consider several important time varying aspects of each level of organization.

The habitat of an organism is the place where it lives, i.e., all of the non-biotic characteristics of the organism's environment. One of the important dynamic considerations, which is briefly discussed above, is the organism's response to changes in the environment. Of particular interest is the concept of tolerances. A complex of conditions are prerequisite for the success of a given organism in a specific area. For each of these conditions the organism has a range of tolerance. The tolerance ranges define the limits of environmental change which the organism can withstand. Some tolerance ranges may be very wide ("eury-") and others may be very narrow ("steno-"). For example, cod, an important finfish in the Gulf of Maine, spawn in a range of temperatures between  $41^{\circ} - 47^{\circ}$  F. Any condition which actually approaches or exceeds the tolerance limits of an organism is said to be a limiting factor. In most cases the limiting factor(s) shift from one variable to another. In marine environments light, temperature and salinity are the three most important factors. However, various chemical

substances may also be important. The particular tolerance ranges of an organism usually depend on the environment for which the individual is acclimated. Species with wide geographical ranges almost always develop locally adapted populations that have tolerance ranges adjusted to local conditions.

Another important dynamic characteristic of individuals is reproduction and life cycles. Reproduction is the single most important function for the individual. Many strategies have evolved for maximizing the success of reproduction. Some of these are more appropriately discussed in the context of population dynamics. The dynamics of interest at this point is the life cycle or developmental steps from adult to fertilized egg to larval and juvenile stages to adult. The specific sequence of steps varies from species to species. Typically the individual at each stage has different tolerance ranges, feeding characteristics, habitat, and trophic position. Therefore, the criteria for success of survival vary as the egg develops to an adult organism. Fortunately, major variations in survival can often be explained on the basis of one or two limiting factors. A single stage may be crucial in the life history of the organism. These variations may be extremely important, but very difficult to quantify in assessing impact of environmental changes.

A population is a collection of individuals of the same or similar species in a specific area. The population has important dynamic characteristics that are not characteristic of the individual, but rather the collective expression of the individual dynamics. Of primary interest are the numbers of a population and the causes and characteristics of fluctuations in the population. The birth rate (natality), death rate (mortality) and dispersal are the most important processes determining population size

and age distribution, i.e. the numbers of individuals in various age classifications.

Dispersal is a crucial process in many species. Movements help prevent overpopulation of areas and allow the population to be larger. Movement and dispersal may be part of the behavioral pattern of the adults such as pelagic finfish. Another form of dispersal is the emission of floating eggs by sedentary organisms. Although spatial heterogeneity plays a central role in population dynamics it is very difficult to describe quantitatively. Data are difficult to obtain and theoretical analyses are very complicated for even the simplest problems.

Mechanisms of population control by changes in natality or mortality are better understood and easier to describe. The importance of limiting factors for individuals has been discussed previously. Similarly, various factors may limit birth and death rates. For any particular species there is a maximum possible rate of birth and death, which is rarely observed due to limiting conditions. Limiting conditions may be density dependent or density independent according to the role of the population itself. The most important limiting conditions include weather, food supply, other populations (competitors or predators), space, habitat characteristics and intrinsic population variables, especially age distribution.

Regulation of population size results from not only variations in natality and mortality, but also the so-called carrying capacity of the environment. That is, the maximum number of individuals which the environment can support. Space and food are the two most common limitations on carrying capacity. Competition with other populations may also be important.

Birth rate (b) and death rate (d) may be combined into a single variable called intrinsic rate of increase, r(r = b - d). Also, carrying

capacity can be designated as K. We can then speak of r and K "strategists". That is, populations may adopt regulation strategies which depend upon increasing r or increasing K. As an example, most marine invertebrates are r strategists, producing many more offspring (high potential r) than can possibly be supported in the environment. On the other hand, birds and mammals are typically K strategists, i.e. maximum r is low, but chances of survival to adulthood are reasonably high. For an r strategist a few surviving adults can produce enough young to maintain and increase a population. However, a K strategist is dependent upon maintaining a relatively large reproducing population.

The next level of organization to be considered is the community. Figure 3-5 illustrates the ways in which two populations may interact.

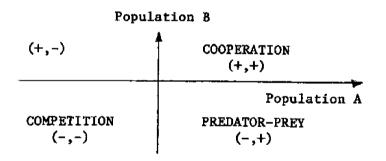


Figure 3-5

Competition and predator-prey relations produce the most important dynamics. These relations are evidenced in the food web diagrams of Figure 3-4. Competition may be indirect as in a food chain or direct via inhibition of one population by another by, say, introduction of toxic substances. Predatorprey relations are the direct result of feeding habits. If a predator has a highly specialized diet i.e., only one prey, then changes in the prey population may drastically effect the predator. However, if the predator

has a diverse array of prey, then the predator is only loosely coupled to any single prey.

Ecosystem dynamics are based on the flow of energy and cycling of materials. Most importantly is so-called ecological succession, the orderly process of community development that involves changes in species structure and community processes with time. Succession results from changes in the physical environment, especially community-controlled changes. Succession is especially important due to the final configuration of the ecosystem, called a climax community, which tends to be well-balanced and highly stabilized. Succession may be interrupted or arrested by environmental perturbations, such as weather variations.

Short-term, periodic sequences in dominant populations are called seasonal successions. Most common is the so-called Spring-Autumn phytoplankton succession in marine waters. Variations in temperature, light and nutrients result in a sequence of phytoplankton populations in which a particular species derives a short-term competitive advantage and therefore dominates the other species.

The preceding discussion has been brief and incomplete. However, the basic principles of ecology are outlined and sufficient basis for assessing impacts of environmental changes developed. The complexity of the relationships outlined is difficult to deal with in the real world. Many uncertainties and information gaps exist. The most important of these relative to this study are outlined in the next section.

3.3 Information Needs and Synthesis for Assessing Environmental Vulnerability

In the two previous sections the processes contributing to the impact of environmental modifications and the basic ecological principles have been reviewed. This information can now be integrated into an overall

assessment framework. Figure 3-6 illustrates the information inputs and synthesis which must be achieved to assess the environmental vulnerability of Machias Bay, Maine to an oil supertanker terminal.

Environmental vulnerability as used herein denotes a qualitative characteristic expressing the liability to biological change of a specific region (such as the Machias Bay region) relative to a specific activity which may produce environmental modifications (such as an oil supertanker terminal). Vulnerability encompasses both the extent of possible biological change that may take place and the probability with which that change may occur, given that the specific activity of interest is implemented. Biological changes at all levels of biological organization, especially the ecosystem, must be considered. Therefore, modifications of physical variables, i.e., habitats, are included.

A distinction is made here among vulnerability, effect or impact, and sensitivity. The specific effects or impacts of events are the actual or predicted changes that take place, but does not include the probability of change expressed in the concept of vulnerability. Sensitivity refers to individual organisms and specific modes of response to changes in environmental quality. Sensitivity is typically expressed in terms of critical concentrations or ranges of concentration of substances such as oil.

Note that the desirability or undesirability of a particular change has not been discussed. The attachment of values to particular changes must be part of the actual decision to undertake any proposed activity. A clear distinction should be made between assessing environmental vulnerability and the decision to select among alternative courses of action. The latter requires adoption of a value system, which must include inputs from many interest groups. The purpose of this report is to provide as

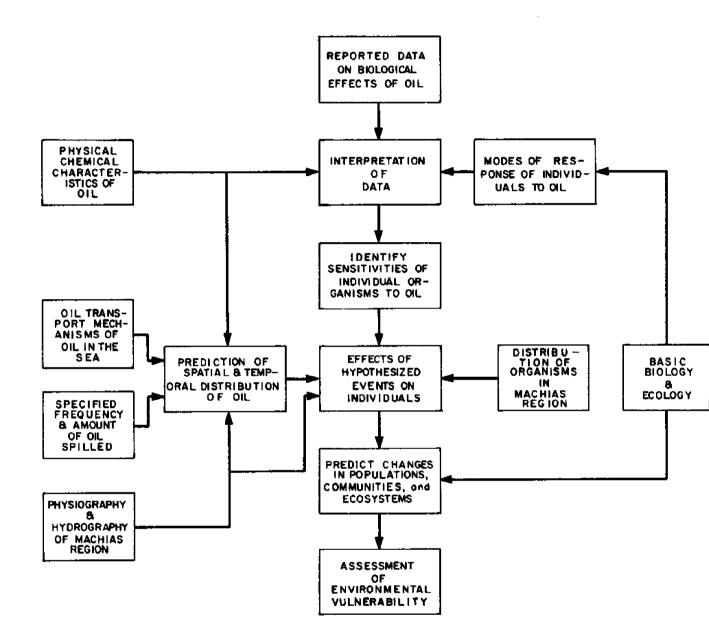


FIGURE 3-6 INFORMATION INPUTS AND SYNTHESIS FOR ENVIRONMENTAL VULNERABILITY ASSESSMENT OF MACHIAS BAY, MAIN, TO OIL SUPERTANKERS

scientific a basis as is reasonably possible for determining environmental vulnerability, from which sound decisions can be made.

Figure 3-7 summarizes the information needs identified in Figure 3-6 for assessment of the potential impacts of oil supertankers on Machias Bay, Maine. The four major categories of information needed are: 1) definition of existing conditions; 2) specification of proposed environmental changes, including input characteristics, transport mechanisms and physical/chemical properties of foreign substances; 3) definition of organism responses to hypothetical environmental changes; and 4) understanding of ecologic processes and "cascading" effect of individual responses on population, community and ecosystem structure and dynamics. Ideally, this information is synthesized using a mathematical model, which allows the exploration of numerous hypotheses and scenarios. However, the levels of uncertainty (as for the case at hand) may prevent implementation of usable models. The following paragraphs indicate some of the important sources and implications of uncertainty in this problem.

#### 3.3.1 Definition of Existing Conditions

Exact descriptions of the existing environment are impossible to develop and are not needed. However, it is important to have some detailed knowledge about the physical, chemical and biological characteristics of the system. Static descriptions of "what is there" are usually the best known. The species of fish, invertebrates, phytoplankton, etc. can be obtained using data from the specific area of interest and other similar areas. The dynamics of the system variables and spatial patterns of distribution are usually much less well-known. The hydrodynamics (current structure), temperature distributions, spatial distribution of fish, competitive interactions and food chain relationships are examples of information which is often unknown or at least very uncertain.

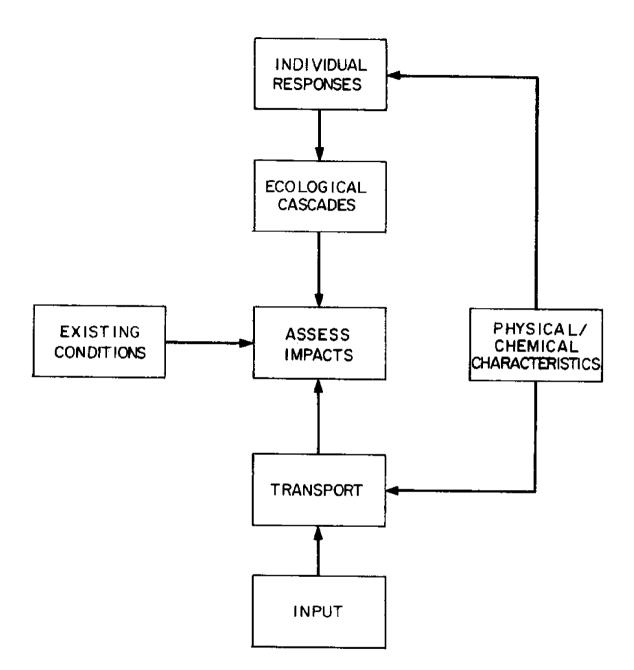


FIGURE 3-7 INFORMATION REQUIREMENTS FOR ENVIRONMENTAL IMPACT ASSESSMENT.

Of particular importance in assessing effects of man-made environmental changes is the ability to distinguish between impacts of man-induced changes and "natural" environmental fluctuations such as temperature and salinity. Reproductive processes and larval survivorship are strongly coupled to currents, temperature and meteorologic events. However, predictive descriptions of these relationships are undeveloped.

# 3.3.2 Definition of Proposed Environmental Changes

Specification of amount and temporal and spatial distribution of oil spills and other hypothetical events are treated in detail in other sections. However, it is also necessary to evaluate the physical and chemical characteristics of these inputs. This is particularly true with respect to oil because of its complex composition. The importance of recognizing the chemical properties of materials introduced in the environment is discussed in Section 3.1. Often the chemistry of materials is reasonably well-known. However, uncertainties arise in specifying the transport and modifications which take place in the specific environment. Important hydrodynamic and meteorologic processes are not fully understood. The problem is compounded by the importance of knowing the spatial patterns which are again difficult to determine.

## 3.3.3 Determination of Specific Biologic Responses

In order to make reasonable impact assessments, it is, of course, necessary to know the response of individual organisms to the expected environmental changes. This information is typically not well-known. Laboratory bioassay tests are fraught with problems, especially lack of standardization. Field data describing observed events are incomplete and because of different sampling procedures at different events, it is difficult, if not impossible, to make comparative analyses. Furthermore,

adaptive mechanisms of organisms produce individuals which are acclimatized to local environments. Individuals of the same species from different localities may respond differently to the same environmental change.

The problem is further complicated when one considers the effects of individual responses at the population, community and ecosystem levels. Organizing principles for the various levels of organization are not well understood. The structure of the system may be identifiable, but answers to the question of <u>why</u> one species or set of species exist and not another are unknown. A particularly important question of population dynamics is also unclear. What is the linkage between adults, natality, larval survival and ultimate population fluctuations and dynamics? Furthermore, what is the effect of "natural" environmental perturbation on population levels? Answers to these questions are necessary to make definitive impact assessment. Finally, there is once again the question of adaptations and successions at the community and ecosystem level. Fundamental principles and answers to questions of "why" are extremely fuzzy.

In spite of these sources of uncertainty it is necessary to utilize the information that is available to make as clear an assessment of impacts as possible. In the process some of the uncertainty will be alleviated and new questions will be posed. In the future, additional information will be gathered and should be used to update old solutions.

#### 4. DESCRIPTION OF EXISTING CONDITIONS -THE EASTERN COAST OF MAINE

4.1 Physical Description

4.1.1 Coastal Physiography

The physical features of the coast of New England are the result of the glaciers which covered North America several thousand years ago. Southern New England was the farthest limit reached by the last glaciation, and deposits of the glacial till, which was scraped off the terrain to the north, form conspicuous topographic features along the coast. A line of these morainal deposits forms the backbone of Long Island, Cape Cod, Martha's Vineyard, and Nantucket. This moraine extends out under water on the continental shelf, and forms Georges and Browns Banks, two relatively shallow glacial deposits on the edge of the shelf.

The New England coast is composed of two types: rocky and sandy. The point of division occurs near Portland, Maine. North of this point, glacial erosion has stripped away most unconsolidated sediment, gouging out valleys and rounding off mountains in the process. The rocky, irregular coast northeast of Portland resulted after eroded river valleys flooded as the glaciers melted and sea level rose. To the south, the glacial till of the terminal moraine was spread out as rivers of glacial meltwater formed outwash plains. The broad stretches of sandy beaches in southern New England are the results of this. South of Portland, the stretches of beach are occasionally interrupted by rocky headlands, such as those near Gloucester, Mass., Cohasset, Mass., and Newport, R.I.

Two of the most prominent types of landform which evolved during and after the period of glaciation are the estuary and salt marsh. The estuary is defined by Pritchard (1935) as "a semi-enclosed coastal body of water which has free connection with the open sea and within which seawater is measurably diluted with fresh water derived from land drainage". Most commonly they are mouths of rivers in which seawater and freshwater intermix. Estuaries in New England have been prime centers for human

activity since colonial times. The extremely deverse natural resources of these estuaries make them ideal for settlement. Although much abused, estuaries still serve crucial links in the life cycles and food webs of coastal ecosystems.

Salt marshes are estuaries which have partially silted in, leaving mud or sand flats which are colonized by hardy <u>Spartina</u> grasses. These grasses provide stability to the substrate, and slow down water movement, allowing deposition of more sediment, thus enlarging the marsh. The decaying <u>Spartina</u> grasses provide food for an extremely rich ecosystem; many oceanic organisms depend on estuarine productivity for at least part of their life cycles.

A wide variety of benthic substrates along the coast are irregularly distributed. For instance, in Cape Cod Bay, patches of gravel are found adjacent to areas of fine silt and clay. On Georges Bank, Wigley (1961) charted benthic particle size distribution, and found no regular distribution pattern. Thus, it is difficult to give a general description of benthic substrates along the coast. A few characteristics of sediment distribution are worthy of consideration, though. Larger particle sizes correlate with strong tides and currents, as one might expect, smaller particles are washed away more easily. On the eastern Maine coast, silt and clay bottoms occur with regularity only in protected embayments and estuaries; sand and gravel are more common in areas which are relatively unprotected.

### 4.1.2 Coastal Hydrography and Climate

The gross circulation pattern of the Maine coast is dominated by a large cyclonic gyre in the Gulf of Maine which develops in spring and breaks down by early fall (Figure 4-1). The ebb and flood of tides are thought to provide the driving force for this gyre (Bigelow, 1927). The prevailing westerly winds, spring runoff from 60,000 sq. mi. of drainage area, and Coriolis force all modify this tidal energy into the characteristic counterclockwise pattern. Drift bottle studies (Bumpus & Lauzier, 1965) show a southwest drift along the Maine coast, the exact path of which is

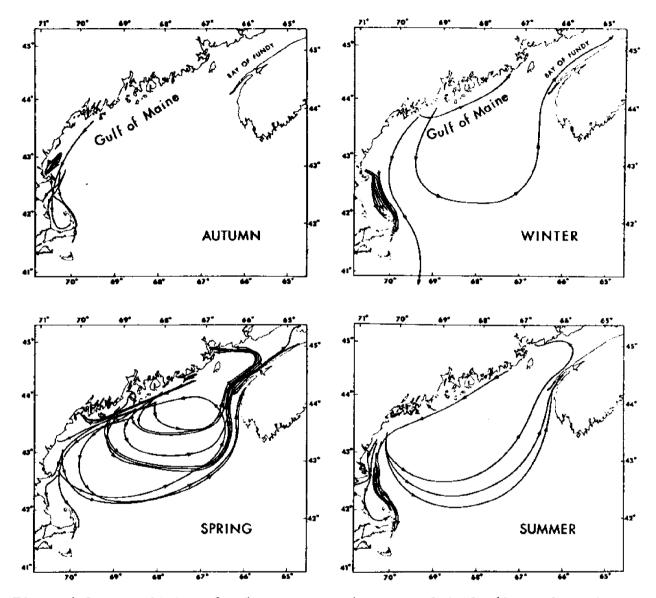


Figure 4-1. Localities of release, assumed routes of drift (drawn from the charts of Bumpus and Lanzier, 1965), and localities of recovery of surface drift bottles released during different seasons, 1963-64. (Graham, 1970)

modified by northwest winds in spring and summer. Graham (1970) confirmed the results of previous drift bottle studies and charted seasonal bottom currents also. Bottom water tends to move inshore into bays and estuaries in winter along the eastern Maine coast, and inshore in summer along western sections of the coast. At the same time, surface waters drift along the coast towards the southwest. Thus, a good deal of upwelling occurs. However, upwelling may not be present when winds, dynamic pressure gradients at the surface, and bottom topographic features combine to direct surface drift shoreward instead of along the coast.

Virtually no data exists concerning the fine structure of near coastal circulation patterns. The irregularity of coastal morphology precludes any general descriptions. Surface runoff, bottom topography, meteorological conditions, and most importantly, tidal flows, all combine to complicate the problem. Current data are available only in the approaches to ports; even so, local mariners rely on their own experience and intuition more than the often inaccurate published current data. Some insight into the speed of local currents can be obtained from an examination of bottom substrate descriptions on U.S. Coast & Geodetic Survey charts. The presence of mud as opposed to gravel may indicate relatively slow currents. Obviously, no information can be obtained about the direction or periodicity of these currents.

River discharge and tidal motion in nearshore waters often combine to produce swift currents. Spring tides range from 11 to 21 feet along the coast. The velocity of these currents is often as high as 2 knots and in constricted areas as swift as 6 knots. The greatest storm surges result from offshore passage of extratropical cyclones. Surges over five feet above mean high water have been experienced.

The weather in the region experiences frequent and rapid changes, especially in the cooler seasons, due to the extratropical cyclones (Nor'easters) which enter the area from the west or southwest. The prevailing westerly winds have a northerly component from November to March, with a southerly component from April to October. Wind speeds are typically 15-20 knots, however, speeds greater than 100 knots have been recorded.

Fog blankets coastal waters frequently, especially in summer. Libby Is. lighthouse in Machias Bay (1/4 mi. from the proposed supertanker terminal on Stone Is.) averages 290 hours of foghorn operation in July (39% of the month) (Brower, et. al. 1972). Air temperatures range from the 70's (F) in the summer to as low as 0°F in the winter. Sea temperatures typically fall between freezing (32°F) and 60°F. A more complete description of climate and meterological conditions in the Machias Bay area may be found in Brower, et. al. (1972).

#### 4.1.3 The Machias Bay Region

The coast of maine near Machias Bay is typical of all rocky coasts in temperate regions. USC & GS Chart 304 (Tibbett Narrows to Machias Bay) covers approximately 135 linear miles of coastline, of which 60 are rocky; the rest is unconsolidated sediment (sand, mud, or gravel), which is typically found in protected embayments. Less than 10 miles of this is sand beach of the type found in southern New England. The many islands within the area of Chart 304 have approximately 120 miles of coastlines, of which 110 is rocky, and only 4 is sand beach, because of the greater exposure of the islands. A handful of small marshes occur in the area, far up in estuaries, protected from Maine's often violent surf. Mud and sand flats, a habitat for valuable clam and worm resources, are found in less protected estuarine areas and coves. A few thousand acres of flats occur within the area of Chart 304.<sup>1</sup>

4.2 Biological Description of the Coastal Waters of Maine

### 4.2.1 Intertidal Communities

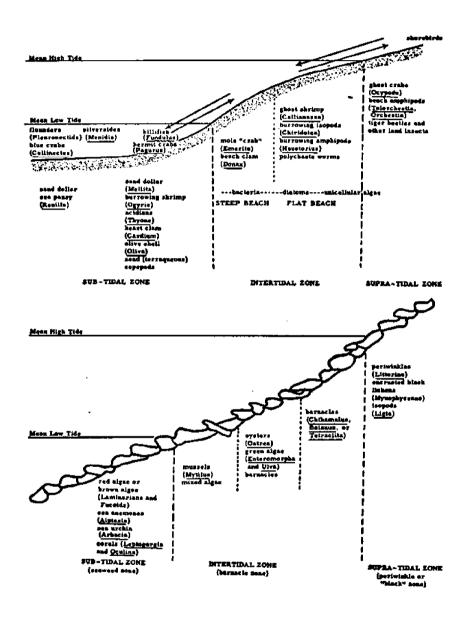
As described earlier, the coast of Maine is dominated by rocky intertidal shores in exposed areas, with areas of unconsolidated sediment being present in bays and estuaries. The rocky intertidal shore exhibits well-defined zonation in flora and fauna, due to the gradient of environmental effects due to the ebb and flood of the tides. This zonation conforms to "textbook" descriptions of temperate rocky intertidal shores throughout the world (see for example, Moore, 1958; Odum, 1971). Figure

<sup>&</sup>lt;sup>+</sup>These estimates are made by direct measurements from USC & GS Nautical Chart No. 304

4-2 describes the distribution of animals and plants on a typical rocky shore. With reference to Maine, the zone just beyond the reach of the tides, but still subjected to sea spray, is dominated by encrusting lichens and herbivorous gastropods (the periwinkle Littorina littorea being the most abundant). Below this, at the high water mark is a band dominated by the barnacle Balanus balanoides, which completely covers all rock surfaces. The edible mussel Mytilus edulis occupies the zone immediately below the barnacles. Depending on the degree of exposure to surf action, rockweeds (Fucus sp.) grow in the zone with the mussels. Near the low water mark, red algae such as <u>Chondrus crispus</u> predominate. Below the low tide mark, laminarian algae (kelp) such as Alaria sp. grow with the red algae. This whole zonation occurs over a vertical distance of about ten feet; some zones are frequently a foot or less in width. The seaweed forest provides food for a diverse invertebrate fauna, including gastropods such as periwinkles, dog whelks (Thais lapillas), and limpets (Acmaea sp), echinoderms like starfish (Asteria sp.) and sea urchins (Strongylocentrotus drobachiensis), and many small arthropods such as amphipods. <u>Chondrus</u> crispus, the sea moss is harvested commercially; 114,000 lb. were harvested in the Jonesport-Machiasport area in 1969. In addition, studies on the feasibility of harvesting blue mussels (Mytilus edulis) are underway; an estimated 300,000 bushels of marketable mussels exist in Hancock and Washington Counties.

If the zonation is modified or disturbed in some manner, several years are often required for a complete recovery. Castenholtz (1967) reported that <u>Mytilus californianus</u> had not recolonized a transect of rock that had been cleared of all organisms five years before. Exposure to a pollutant could have similar consequences.

In intertidal areas composed of unconsolidated sediments (mud, sand, or gravel), few plant species are found (salt marshes are the exception; they will be discussed in the context of the estuarine habitat). However, the fauna are usually quite diverse (Figure 4-2). Arthropods such as burrowing amphipods and ghost shrimp and a wide variety of polychaete worms and bivalve mollusks inhabit sand and mud intertidal areas. Of great commercial importance on mud and sand flats are bloodworms (<u>Glycera dibranchiate</u>; worth more per



а.

Figure 4-2

Transects of a sandy beach (upper) and rocky shore (lower). (from Odum, 1971)

pound wholesale than lobsters), sandworms (<u>Nereis vinens</u>), and soft-shell clams (<u>Mya arenaria</u>).

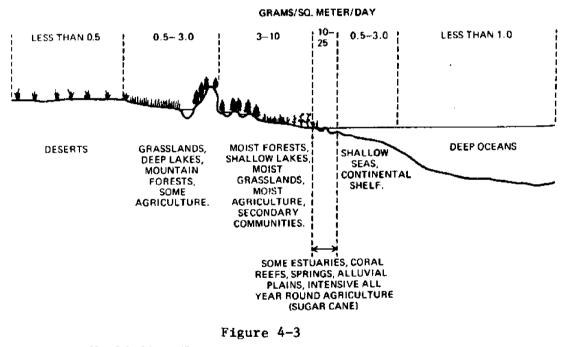
Estuaries and salt marshes are of immense importance to marine ecosystems. Estuarine primary productivity (Figure 4-3) is among the highest on earth. The average estuary and salt marsh (considered together since they are interdependent) produces 10 tons of dry materials per acre per year.

Estuarine marshes are found along the entire coast. Most New England marshes and those of Long Island Sound that are developed on rivers and near inlets experience tidal changes in water level. The extensive wetlands that fringe the almost tideless coastal lagoons have a horizontal circulation of water caused by tidal currents, winds, and freshwater runoff, but changes in water level occur primarily in connection with storms or the prolonged press of winds from any one direction.

Marshes are transitional. Their initial formation requires a substratum bare for about half the tidal period; water calm enough to prevent the uprooting of the plants, and a sufficient supply of sediment to enable the upward growth of the marsh to keep pace with or exceed the rise in sea level due to glacier melt. Variation in substratum, drainage, aeration, and tidal cycling in addition to salinity produce a wealth of community subdivisions. The dominant species are usually botanical.

In quiet, submerged shallows the eel grass, <u>Zostera</u>, and another seed plant, <u>Ruppia</u>, dominate. Most of the invertebrates of the <u>Zostera</u> community actually are common on soft-ground habitats, but the population density is probably greater in the presence of eel grass. Among the swimmers and crawlers are several amphipods, the shore shrimp <u>Palaemontes</u> and <u>Crangon</u>, many snails and bivalves and a long list of worms.

<u>Spartina alterniflora</u> is the dominant grass in the mid-tidal area of the marsh. A typical assemblange at the lower <u>alterniflora</u> level illustrates the ecotonal qualities of the marsh as a transition between hard- and soft-ground communities. The ribbed mussel <u>Modiolus</u> is a dominat form providing a base



World distribution of primary production. (Murdoch, 1971)

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of attachment for estuarine barnacles, bryozoans, anemones, and the fucoid seaweeds. Throughout its range, which extends north through New England, the Modiolus assemblage includes a variety of small invertebrates.

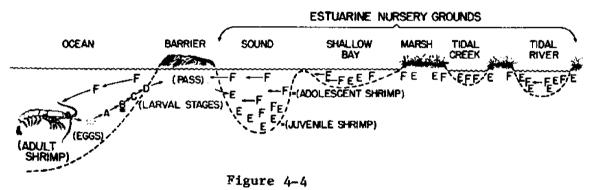
<u>S. alterniflora</u> grows in the upper two-thirds of the littoral but is supplanted at elevations equal to or exceeding mean high water by high marsh communities. Plants growing at this level tolerate short-term daily submergence but require only a few wettings per month. This higher zone is dominated by short cord grass, Spartina patens.

Higher marsh associations harbor periwinkles and a characteristic snail, <u>Melampus bidentatus</u>, plus an assortment of salt marsh beetles, dipternaš, and other essentially terrestrial arthropods. Fiddler crabs develop extensive colonies at the same level on bare flats or in eroding banks adjacent to marsh areas. A terrestrial fauna with crickets, earwigs, termites, and other small arthropods. The "marine" contingent is represented ` here by salt marsh beach fleas, which are intolerant of prolonged or frequent submersion in water.

Many species use estuaries as spawning or nursery areas. Graham (1972) described the migrating behavior of herring larvae in anestuary which keeps them from being carried out into less productive open waters. They ascend to the seaward-flowing surface waters at the head of the estuary, drift to the estuary mouth, then migrate to the bottom where they drift upstream with bottom currents back to the head of the estuary. Figure 4-4 illustrates the role of the estuary/marsh complex as a nursery ground. The sequence of events for the shrimp is typical for many coastal invertebrates. Various birds also rely on estuaries for food and rest while migrating, and for a habitat while breeding.

Salinity, temperature, sediment distribution, and water circulation are the primary factors determining the distribution of organisms within an estuary or salt marsh. Modification of any one of these can destroy the biological community present in the marsh or estuary. Many of these changes like Hurricane Agnes which flooded the Mid-Atlantic states and lowered the salinity of Chesapeake bay, wiping out hundreds of square miles of clam and oyster beds, are natural in origin, but many others are caused by man.

Channel dredging and filling, once thought to be harmless, has caused the erosion of thousands of acres of salt marsh by changing the flow rates and



Life history of shrimp that use estuaries as nursery grounds. Adult shrimp spawn offshore and the young larval stages (A, nauplius; B, protozoea; C, mysis; D, postmysis) move shoreward into the semienclosed extuaries where the juvenile (E) and adolescent (F) stages find the food and protection they need for rapid growth in the shallow bays, creeks, or marshes. The maturing shrimp then move back into the deeper waters of the sounds and adjacent ocean where they are harvested by commercial trawlers. (Odum, 1971)

directions of channels. The upriver diversion of water for irrigation has increased the salinities of many small estuaries.

## 4.2.2 Subtidal and Pelagic Communities

The distribution of subtidal benthic species is related to the nature of the substrate. Gravelly or sandy bottoms are usually inhabited by filter feeders. Crustacea such as amphipods, most bivalve mollusks, and various coelenterates all either burrow into or settle on these substrates. Detritus feeders (which swallow the substrate, digest whatever organic material happens to be present, and excrete the rest) inhabit clay-silt bottoms. Most prominent among these are some polychaete worms.

Wigley (1961) surveyed the benthic fauna of Georges Bank. Striking correlations were observed between the type of bottom sediment and the quantity of benthic organisms. High abundance was associated with coarse sediments, and low abundance was associated with fine sediments. By far the greatest faunal weight was found in gravel and sandy gravel bottoms. The biomass in the sandy gravel sediment was exceptionally high (1300  $\text{gr/m}^2$ ), due largely to the occurrence of dense beds of <u>Modiolus modiolus</u>, the northern horse mussel. Low quantities occurred in sediments in which the sand fraction was dominant. Lowest weight were found in clayey silt and silty clay bottoms.

The relation of numbers of specimens to sediment classes was quite similar to that for weight. Greatest numbers of specimens were found in gravels and sands; fewest specimens occurred in sediments containing large quantities of silt and clay. Organisms were most abundant  $(1934/m^2)$  in the sand textural class. Gravel, sandy gravel, and gravely sand also rank high, with the number of specimens ranging from 1513 to  $1718/m^2$ . Except for the clayey sand category, in which the number of specimens averaged  $1074/m^2$ , the remaining textural classes (silty sand, sand-silt clay, sandy silt, clayey silt, and silty clay) supported few specimens - 255 to  $436/m^2$ .

There were three areas of the Bank where a high density (>100  $gm/m^2$ ) of benthic animals occurred; the northeast, south-central, and western. The first two of these areas each consist essentially of one large contiguous

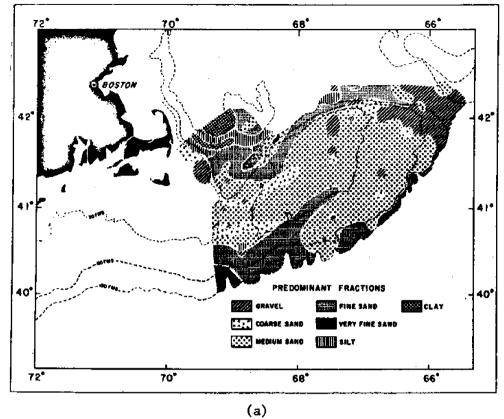
area, whereas the third is a cluster of six relatively small high-density patches. (Figure 4-5a and b).

Each major faunal component has a somewhat different and distinct geographic density pattern. Crustaceans are most prevalent along the western and southeastern parts of the bank; moderate quanities occur in the northeast and southern sections. Mollusca are most abundant on the northeast, south-central, and western portions. Echinoderms are especially dense in the central portion, with moderate quantities occurring on the bank's northeast, northwest, and south-central parts. Annelids are prevalent on the northeastern, south-central, and western sections. Annelida are the only group abundant in Georges Basin, the deep-water area northwest of Georges Bank. The benthic fauna of the Bank are composed by weight of the following groups: Molluscs 41%, Echinoderms 31%, Miscellaneous groups 17%, Annelids 6% and Crustaceans 5%.

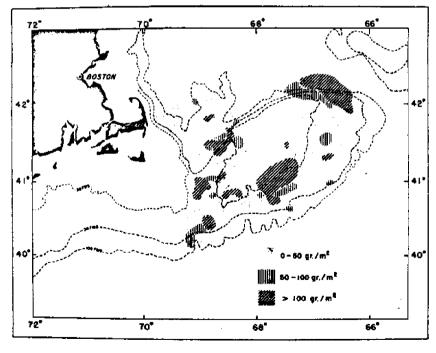
The same sort of distributions are found in near shore waters. The highly productive gravel bottom also serve at spawning grounds for demersal fish close to shore, cod spawn in Massachusetts Bay over gravel areas off Gloucester and Plymouth, Massachusetts.

Many near-shore subtidal benthic organisms are of great economic importance. Coastal populations of the American lobster (<u>Homarus americanus</u>) tend to stay near the highly productive estuary areas in the summer; they move slightly offshore in the winter months. Maine lobster fishing is generally carried on within the 25 fathom contour the year round. Bay scallops migrate into the area seasonally, and are also sought by commercial fishermen.

The pelagic near-shore community differs little from that found in the seaward waters of the Gulf of Maine. The phytoplankton and zooplankton populations are described in detail by Bigelow (1924), as are finfish by Bigelow and Schroeder (1953). Some of the organic detritus found on the bottom near shore results from dead plankton remains, although the majority comes from detached seaweeds and grasses of the intertidal zone.



Geographic distribution of sediment fractions.



(b)

Geographic distribution of benthos.

Figure 4-5 (from Wigley, 1961)

5. COMPOSITION AND CHARACTERISTICS OF CRUDE PETROLEUM AND PETROLEUM PRODUCTS 5.1 Introduction

Crude petroleum is a complex mixture of hundreds of chemical compounds derived from biological matter which has accumulated in reservoirs in the earth and been subject to physical and chemical processes extending over millions of years. Petroleum from different geographical areas generally contains the <u>same</u> compounds but with different percentage composition. Because the biological effects of groups of similar compounds vary significantly, it is essential to consider the <u>relative abundance</u> of the various compounds in a particular crude oil or in a petroleum fraction which enters the environment.

In order to unambiguously describe and distinguish between the many organic compounds, a standard organic chemistry nomenclature has been established. This naming system and a very brief introduction to organic chemistry are discussed before describing crude petroleum. With this information, the type of an organic compound and general characteristics can be identified from the compound name.

5.2 An Introduction to Organic Chemistry

All organic compounds are composed of hydrogen and carbon; some also contain oxygen, nitrogen, sulfur, and a variety of other less common elements. Ring compounds with oxygen, nitrogen, sulfur or trace metals in their ring structures, are called heterocyclic compounds. Because most of the compounds encountered in crude oil contain only carbon and hydrogen, detailed discussion will be limited to these.

The properties of a compound (boiling point, solubility in water, etc.) depend on the different elements present, the number of atoms of each element in the molecule, and the structure that is formed when the atoms of each element in the molecule, and the structure that is formed when the atoms of each element in the molecule, and the structure that is formed when the atoms bond together. The empirical formula of a compound,  $C_{x y}$  (where x is the number of carbon atoms and y is the number of hydrogen atoms), provides the number of atoms present, but says nothing about the structure they form. Actually, for any given  $C_{x y}$ , there are usually many

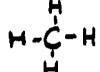
possible structures, each having different properties. Thus, use of the empirical formula does not provide an unambiguous way of distinguishing between hydrocarbon molecules.

An internationally standardized systematic method for naming hydrocarbons has been developed which can distinguish between any two structures. Unfortunately, some compounds were named before their structures were analyzed, so they have non-systematic names, which are still used.

A carbon atom has the ability to form four bonds to other atoms (not necessarily carbon), while a hydrogen can bond to only one other atom:



The simplest hydrocarbon is methane:



which has the empirical formula  $CH_4$ . (Note that there are no possibilities for other structures with the same empirical formula).

Ethane,  $C_{2}H_{6}$ , is next in this series:

Table 5-1 indicates the general trends of this series of hydrocarbons. Molecular weights increase by about 14 units as each CH<sub>2</sub> unit is added. Boiling points increase as molecular weight increases (note that pentane is the smallest molecule which will remain a liquid at room temperature). The solubility data also reflects this. The value is normally given in grams of the hydrocarbon which will dissolve in a million grams of water at room temperature, but for methane, ethane, propane, and butane (which are gases at room temperature and pressure) the value is given in cubic cm. of the gas per 100 ml of water.

A pattern is also apparent in the names and empirical formulas. All the empirical formulas fit the pattern  $C_n H_{n-2n+2}$ . Also, all the names end in -ane. The class of all compounds which have formulas of the form  $C_n H_{2n+2}$ 

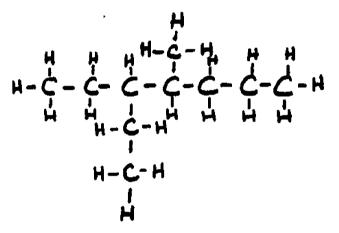
Empirical		Molecular	Standard	Boiling	
Formula	Structure	Wt.	Name	Pt.	Solubility <sup>2</sup>
CH4	4-C-+	16.04	Methane	-161.5	9cm <sup>3</sup> as a gas
с <sub>2</sub> н <sub>6</sub>	H-C-T-H	30.07	Ethane	-88.3	4.7cm <sup>3</sup> as a gas
<sup>с</sup> 3 <sup>н</sup> 8	H-C-H H-C-H	44.09	Propane	-42.2	6.5cm <sup>3</sup> as a gas
<sup>C</sup> 4 <sup>H</sup> 10	ままままま。 H-Ċ-Ċ-Ċ-Ċ-H	58.12	Butane	5 <sup>°</sup> C	15cm <sup>3</sup> as a gas
<sup>C</sup> 5 <sup>H</sup> 12	etc.	72.15	Pentane	36.2	38.5
<sup>C</sup> 6 <sup>H</sup> 14		86.1	Hexane	69	9.5
C7 <sup>H</sup> 16		100.2	Heptane	98.4	2.93
C8 <sup>H</sup> 18		114.23	Octane	125.8	.66
<sup>C</sup> 9 <sup>H</sup> 18		128.25	Nonane	150.8	.22

# Table 5-1 Structure and Properties of Alkanes

a - in  $cm^3/100ml$  for gases; in grams/10<sup>6</sup> grams otherwise

are called alkanes (or sometimes, paraffins). Accordingly, all compounds in this series end with -ane, and the number of carbons is given by a prefix derived from the Latin word for the number. Hexane has six carbons, for example. Notice that methane, ethane, propane, and butane (which were named before their structures were known) do not obey this rule.

Compounds sometimes have side chains originating in the middle of the molecule. In this case the name of the compound comes from the number of carbons in the longest continuous chain. Side branches are identified by the number of the carbon in the longest chain to which they are attached. For example:

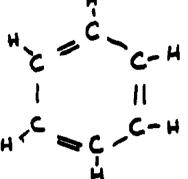


is 3-ethyl-4-methylheptane (-yl replaces -ane when it refers to a side chain). All compounds of this form are known as branched-chain alkanes. Note that these still conform to the  $C_n H_{2n+2}$  type of formula. Unbranched alkanes are commonly known as n-alkanes.

Often alkanes form rings with the formula  $C_{n}H_{2n}$ . The most common of these have 3, 5, 6 or 7 carbons in a ring (cyclopropane, cyclopentane, cyclohexane, and cycloheptane, respectively).

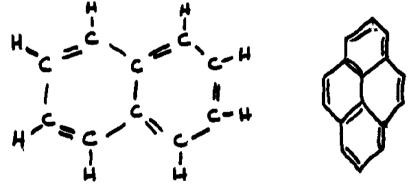
Frequently, double bonds form between carbons. Those compounds having at least one double bond fall into the class called alkenes. These generally do not occur in petroleum (they are common in most animal fats, though). Alkanes are known as saturated hydrocarbons (no double bonds), while alkenes are unsaturated hydrocarbons (at least one double bond in the molecule).

One important type of alkene has the formula  $C_{n}H_{n}$ , and members of this class are known as aromatic hydrocarbons (so named because they evaporate easily, and give off a characteristic scent). Benzene (molecular weight = 78.1, boiling point = 80.1°C, solubility in water = 1780 gm./10<sup>6</sup>gm. H<sub>2</sub>O) is the most common of these:



Notice how its solubility differs from that of hexane, the 6 carbon alkane (Table 5-1). This is a characteristic of all aromatics, as is the ring structure with alternating double and single bonds.

Polycyclic aromatic hydrocarbons (PAH) have two or more aromatic rings:



The number of different combinations that are possible between alkanes, cycloalkanes, alkenes and aromatics probably runs in the millions. Thousands are known to exist in nature, and have been identified and named. Very large molecules, with boiling points above  $400^{\circ}$ C and molecular weights running from 200 to the thousands, are common in crude oil, and are composed of combinations of many classes of hydrocarbons. These are called residuals (the "left-overs" after refining) and form tar or asphalt used to pave streets.

#### 5.3 Composition of Petroleum

The composition of crude petroleum is usually described in terms of hydrocarbons (compounds containing only carbon and hydrogen) and nonhydrocarbons (organic compounds containing sulfer, oxygen, nitrogen or trace metals). Figure 5-1 illustrates the relative abundance of these compounds in two different crude oils. The hydrocarbons are the principal constituents usually exceeding 75%.

#### 5.3.1 Hydrocarbons

Hydrocarbons found in crude oil may be classified as:

- normal paraffins (n-alkanes)
- 2) branched chained paraffins (iso-alkanes)
- 3) cycloparaffins (cycloalkanes)
- 4) aromatics
- 5) naphtheno-aromatic (containing both aromatic and cycloalkane rings)

The relative composition in terms of increasing molecular weight is illustrated in Figure 5-2. The most dramatic change is the increase of naph theno aromatic compounds with increasing boiling point and the relative reduction of normal and branched chained paraffins. The range of hydrocarbon composition is shown in Figures 5-3 and 5-4. The distribution of hydrocarbons types by number of carbon atoms illustrates the wide variations that may occur.

<u>Normal paraffins</u> containing from 1 to 35 carbon atoms  $(C_1 - C_{35})$  have been confirmed although compounds up to  $C_{78}$  have been identified. Paraffins can make up to 25% of the composition of a crude petroleum. They tend to predominate in the low boiling  $(40^{\circ} - 230^{\circ}C)$  portions of crude oil. They usually have a large number of different configurations due to different positions of the branch. <u>Cyclo paraffins</u> may constitute from 30 to 60% of the composition of petroleum. Although the relative abundance of cycloparaffins does not change with boiling point (Figure 5-2) the type of compounds may differ from crude to crude. The principal change is the number of rings. Single cyclo-naphthenes form a major part of the cycloparaffins although 2 to 6 rings are not unusual, and even 10 rings can be found in lubricating poils. <u>Aromatic compounds</u> contain one or more rings but have quite different

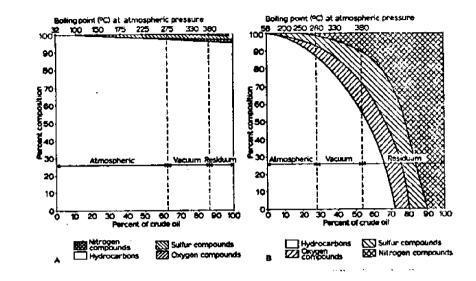


Figure 5-1 Distribution of non-hydrocarbon components in two different crude oils. A = Ponca City crude oil; B = Wilmington crude oil. (Constantinides and Arich, 1967)

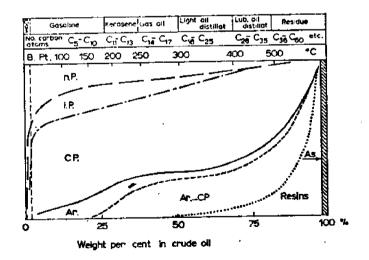


Figure 5-2 Distribution of hydrocarbon classes in a medium crude oil. n.P. = normal paraffins; i.P. = iso-paraffins; CP. = cycloparaffins; Ar. = aromatics; Ar.-CP. = naphtheno-aromatics; Resins = heterocyclic compounds; As = asphaltenes. (Bestougeff, 1967)

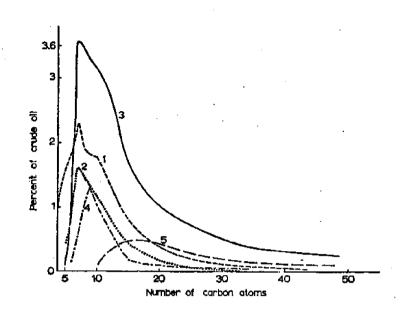


Figure 5-3 Distribution of hydrocarbons in a light (Ordovician) crude oil. (By class and number of carbon atoms per molecule.) (Bestougeff, 1967)

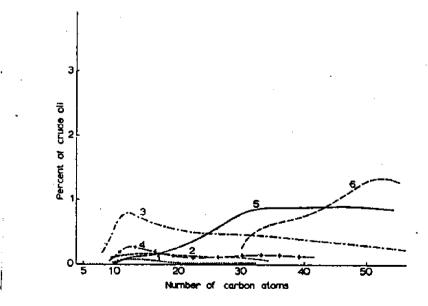


Figure 5-4 Distribution of hydrocarbons in a heavy (Tertiary) crude oil. (By class and number of carbon atoms per molecule.) (Bestougeff, 1967)

properties than cyclohexane or other naphthenes. Benzene and benzene derivatives are major constituents of crude oil. Alkyl benzenes with one or more substituents are the major low boiling constituents. In the higher boiling fractions tri- and polycyclic compounds are present. Polycyclic aromatic hydrocarbons are found in rather small quantities in petroleum (a few fractions of a percent). <u>Naphthenic</u> hydrocarbons and <u>naphtheno-</u> aromatics form a major component of higher boiling petroleum fractions. Most are substituted with the substituted benzene portion having short chains (methyl or ethyl) and the cycloparaffin part longer alkyl chains.

#### 5.3.2 Non-Hydrocarbons

Figure 5-1 illustrates the relative abundance of non-hydrocarbon compounds. Sulfur content may range from 5% up to 30-40% sulfur compounds in heavy crude. It is the most important heteroatom in petroleum and its compounds are found in increasing quantities in the high molecular weight portion of the crude (over 230 C). Oxygen compounds, acids, phenols, ketones, esters constitute up to 2% of crude petroleum. As with sulfur oxygen compounds increase with boiling point, the greatest fraction found in the distillate over 400°C. Nitrogen is present only in 0.01 to 0.2% (a few percent nitrogen compounds). <u>Asphaltenes</u> are heterocyclic substances containing oxygen, sulfur, nitrogen and trace metals with molecular weights in the range of 900-3000. They can represent a significant portion of the crude, from 0 to 20%. Though their composition is not completely known they are essentially layers of condensed aromatic and naphthenic rings containing heterocyclic atoms connected by short n-paraffin chains. Most trace metals are found incorporated in compounds called porphyrins. These compounds, of which chlorophyll is one, are of high molecular weight, and provide a clue to petroleum's biological origins.

5.3.3 Classification by Boiling Point Distribution

An alternative approach to characterizing petroleum is by boiling point distribution. Rather than consider chemical compound types specifically, broad boiling point fractions (distillation fractions) are used, each fraction containing a variety of chemical compounds. This approach has been used by the

American Petroleum Institute and U.S. Bureau of Mines because the classification by boiling point relates directly to industrial fractionation and petroleum products, such as gasoline, fuel oil and lubricants. The relationship between the two methods of classification is illustrated in Figure 5-2 and Table 5-2.

The gas fraction (b.p.<40 C) is of little interest for our purposes. Gasoline boils between 40 to 180 C. It contains n-paraffins from C6 to C12, but also has substantial portions of branched paraffins, cycloparaffins and alkyl aromatics. <u>Kerosene</u> boils from 180<sup>°</sup> to 230<sup>°</sup>C. It contains n-paraffins  $C_{11}$  and  $C_{12}$ , and a substantial proportion of alkyl benzenes, naphtheno-aromatics, and naphthenes (bicycloparaffins). Light gas oil boils between 230° and 305°C and contains n-paraffins from  $C_{13}$  to  $C_{17}$ . Akylbenzenes, naphthalenes, naphthenes and naphtheno-aromatics are major components. <u>Heavy gas oil and light lubricating distillate</u> boils between 305 to 405 C and contains n-paraffins from  $C_{18}$  to  $C_{25}$ . A number of triand tetra-cyclo aromatic compounds are present (napththalenes, anthracenes, phenanthrenes, pyrene, fluorenes), and naphtheno-aromatics such as cyclo-pentenophenanthrene. Increasing percentage of sulfur, oxygen and nitrogen compounds are present. Both diesel fuel and fuel oil are blended mixtures of the boiling point fractions and have similar boiling range, 170°C to 370°C respectively. They include kerosene, light gas oil, heavy gas oil, and light lubricating distillate fractions discussed above. Lubricant fraction boils from 405°C to 515°C and contains very small amounts of  $C_{26} - C_{38}$  n-paraffins. It is essentially naphthenes with 3 to 6 rings, multiple ring naphtheno-aromatics, and heterocyclic compounds.

Smith (1968) discusses the composition of crude oils in terms of boiling point distribution also. However, his terminology and boiling point definition for various fractions is slightly different than that given above, which conforms to API usage.

#### 5.4 0il Weathering

Oil is a complex mixture of many chemical compounds and the characteristi of spilled oil are altered significantly by evaporation, dissolution,

Table	5-2	(Rossini,	1960)
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## Summary of the Amounts of the Broad Fractions Constituted by the Hydrocarbons Isolated from the Representative Petroleum

Broad fraction	Gas	Gasoline	Kerosine	Light gas oil	Heavy gas oil and light lubricating distillate	Lubricant fraction	Resi- due	Total
Boiling range at 1 atm. (°C)	<-10°	40°-180°	180°-230°	230°-305°	305°-405°	405°~515°		
Range of normal paraffins	$C_1 - C_2$	C5-C10	C <sub>n</sub> and C <sub>i2</sub>	C <sub>13</sub> -C <sub>11</sub>		C <sub>26</sub> -C <sub>36</sub>		
Estimated percentage of the original petroleum constituted by the given fraction	4	33.2	12.7	18.6	14.5	10.0	7	100
Number of compounds isolated	7	101	37	12	10	8		175
Estimated percentage of the fraction accounted for by the hydrocarbons isolated	100	82.3	38.4	30.2	20.5	9.9	•••	119
Estimated percentage of the original petroleum accounted for by the hydrocarbons isolated	4.0	27.33	4.8,	3.6 <sub>1</sub>	2.97	0.9 <sub>9</sub>	••.•	45.7

# Distribution, by Class and Broad Fraction, of the Hydrocarbons Isolated from the Representative Petroleum

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						•	
Broad fraction	Gaa	Gasoline	Kerosine	Light gas oil	Heavy gas oil and light lubricating distillate	Lubricant fraction	Total
Boiling range at 1 atm. (°C)	<40°	40°-180°	180°-230°	230°-305°	305°-405°	405°-515°	····
Range of normal paraflins	$C_1 - C_5$	$C_6-C_{10}$	$\mathbf{C}_{\mathbf{n}} = \mathbf{C}_{\mathbf{n}}$	C13=C17	C45-C25	$C_{25} - C_{33}$	
		Nun	iber of Compour	nds			
Classes of hydromychons							
Normal paraffins	5	5	2	5	8 .	8	33
Branched paraffins	2	35					37
Alkyl cyclopentanes		22					22
Alkyl cyclohexanes		13	1				11
Alkyl cycloheptanes		1					1
Bieyeloparattins		4	6			• • •	10
Trieveloparallins			ĩ				10
Alkyl benzenes	!	20	20			• • •	-10-
Aromatic cycloparaffins		ī	6	1			-10-
Dinuclear aromatics			ř.	ĥ	· · ·		2
Trinuclear around ics				• • •	ì	• • •	i
$\mathbf{T}$ otal	7	101	37	12	10		175

microbial and chemical oxidation (Dean, 1968; Blumer and Sass, 1972). Blumer and Sass (1972) and Blumer, et. al. (1972) have recently reported data which clearly demonstrate the extent of these various degradation processes. Because the varying constituents of oil are affected at different rates by these "weathering" forces the relative composition (and therefore biological effects) of the spilled oil also varies.

The large number of individual compounds in crude oil precludes the consideration of the weathering of each one separately. Alternatively, compounds are grouped according to number of carbons and hydrocarbon type in boiling point ranges that correspond closely to the product calssification of API (Table 5-2). Table 5-3 summarizes this grouping and indicates estimates of the range of physical/chemical constants for each fraction. The eight fractions selected provide flexibility in characterizing oil, especially with respect to biological effects both short- and long-term, without confusing the problem with excessive data. More detailed breakdowns are possible and could be warranted in some cases. The role of each weathering component is briefly described below (Blumer, 1970).

Evaporation depletes the lower bailing components (fractions 1, 3 and 5, Table 5-3) but leads to little or no fractionation between hydrocarbons of the same bailing point that belong to different structural series.

<u>Dissolution</u> also removes preferentially the lower molecular weight components of an oil. However, aromatic hydrocarbons have a higher solubility than n-paraffins of the same boiling point.

<u>Biochemical (microbial) attack</u> affects compounds within a much wider boiling range than evaporation and dissolution. Hydrocarbons within the same homologous series are attacked roughly at the same rates. Normal paraffins are most readily degraded. In gas chromatograms this type of degradation manifests itself as a lowering of the ratios between straight chain and adjacent branched paraffins. Extended biochemical degradation then results in gradual removal of the branched alkanes. Cycloalkanes and aromatic hydrocarbons (fractions 3-8) are more resistant and disappear at a much slower rate.

<u>Chemical degradation</u> processes of oil during weathering are not well understood. However, the overall result appears analogous to that

			SPILL W	SPILL WEATHERING MODEL	DEL		
Fra	Fraction Description <sup>a</sup>	% by wt. <sup>a</sup> in Crude Oil	Density <sup>b</sup> (gm/ml)	Boiling Point <sup>b</sup> ( C)	Molecular Weight <sup>b</sup>	Vapor Press. <sup>b</sup> @ 20 C (mm)	Solubility <sup>C</sup> (gm/10 <sup>6</sup> gm Distilled H <sub>2</sub> 0)
П	Paraffin C <sub>6</sub> -C <sub>12</sub>	.1-20	.6677	69-230	86-170	1101	9.501
7	Paraffin C <sub>13</sub> -C <sub>25</sub>	0+-10	. 77 78	230-405	184-352	.1	.01004
ςΩ	Cycloparaffin C <sub>6</sub> C <sub>12</sub>	5-30	.759	70-230	84-164	100-1.	55-1.
4	Cycloparaffin C <sub>13</sub> -C <sub>23</sub>	5-30	.9-1.	230-405	156–318	10	10
ŝ	Aromatic (Mono- and di-Cyclic) C <sub>6</sub> -C <sub>11</sub>	0-S	.88-1.1	80-240	78-143	721	17800.
9	Aromatic (Poly-Cyclic) C <sub>12</sub> <sup>-C</sup> 18	0+-5	1.1-1.2	240-400	128-234	0-1-0	12.5-0
2	Naphtheno-Aromatic C <sub>9</sub> -C <sub>25</sub>	5-30	.97-1.2	180-400	116-300	10	10
Ø	Residual (including hetero- cycles)	10-70	11.1	<b>&gt;400</b>	300-900	0	O
	(footnotes on following page)	ıg page)					

TABLE 5-3

BASIC DATA FOR OIL

SPILL WEATHERING MODEL

#### Table 5-3 (continued)

- a for further detail see:
  - Bestougeff, M.A. in Nagy, Bartholomew and Colombo, <u>Funda-</u> <u>mental Aspects of Petroleum Geochemistry</u>, Elsevier Publishing Company, New York, New York, 1967.
  - 2. Rossini, Fredrick D., <u>Hydrocarbons in Petroleum</u>, Journal of Chemical Education, Vol. 37, No. 11, November 1960.
  - 3. Smith, H.M. <u>Qualitatitive and Quantitative Aspects of Crude Oil</u> <u>Composition</u>, U.S. Bureau of Mines Bulletin 642, 1968.
- b taken or estimated from:
  - 1. Handbook of Physics and Chemistry
  - 2. Physical/Chemical Constants for Organic Compounds

c - taken or estimated from:

- 1. Klevens, H.B., <u>Solubilization of Polycyclic Hydrocarbons</u>, Journal of Petroleum Chem., 54:283-298 (1950)
- Peake, Eric, and G.W. Hodgson, <u>Alkanes in Aqueous Systems</u>. <u>II. The Accommodation of C12-C13 n-Alkanes in Distilled Water</u>, J. Am. Oil Chemists' Society, Vol. 44, pp. 696-702, Dec. 1967.
- 3. McAuliffe, Clayton, <u>Determination of Dissolved Hydrocarbons in</u> <u>Subsurface Brines</u>, Chem. Geol., 4(1969), 225-233.
- 4. Gerarde, H.W., <u>Toxicology & Biochemistry of Aromatic Hydro-</u> carbons, Elsevier Publishing, London, 1960.

obtained in technical oxidation processes (e.g. "blowing" of asphalt). Oxidation affects most readily the aromatic hydrocarbons of intermediate and higher molecular weight.

The effect of these weathering processes is the rapid (48-96 hour time period) depletion of lower boiling fractions (boiling point <250°C) from a spilled slick by evaporation and dissolution and slow degradation (in terms of years) of higher boiling fractions by microbial and chemical oxidation. Figures 5-5, 5-6 and 5-7 illustrate the rate at which these weathering processes occur. In Figure 5-5 the loss rate by evaporation and dissolution of C11 hydrocarbons, which is representative of fractions 1, 3 and 5, is illustrated. The data is replotted as a function of wind speed in Figure 5-6. From these figures the total rate of loss can be estimated to be approximately  $.5+.8e^{-2S}$  (in days  $^{-1}$ ) where, S is the wind speed in knots. Temperature also plays an important role, but data to include temperature effects is not available. Figure 5-7 illustrate the microbial degradation of higher boiling fractions using data on  $n - C_{17}$ (heptadecane). Because pristane is not degraded until after  $n-C_{17}$  is oxidized, the ratio of these two is a measure of microbial oxidation. Fractions boiling higher than n-C17 have degradation rates orders of magnitude slower than that obtained for n-C  $_{17}$  ( $\sim$ .01/day).

From the point of view of the biological effects of oil, dissolution is a particularly important weathering process. First, it leads to rapid depletion of spilled oil of significant portions of the highly toxic, low boiling fractions. Secondly, however, the depletion in the slick by dissolution implies presence of these hydrocarbons as dissolved materials in water. Table 5-3 provides sufficient data to compare the solubility characteristics of a wide variety of hydrocarbon mixtures including the crude oils given in Table 2-1, petroleum products and various solvents. Any one of these materials can be characterized by percentage composition of the eight fractions. Using the solubility data it is then possible to estimate the amount of the various fractions that could actually go into solution in any given situation. Table 5-4 summarizes estimates of these data.

FRACTION	DESCRIPTION	CRUDE A	CRUDE B	#2 FUEL OIL	KEROSENEC	BUNKER C
1	Alkanes (C <sub>6</sub> -C <sub>12</sub> )	1	10	15	15	0
2	Alkanes (C <sub>13</sub> -C <sub>25</sub> )	1	7	20	20	1
3	Cyclo- Paraffins(C <sub>6</sub> -C <sub>12</sub> )	5	15	15	20	0
4	Cyclo- Paraffins(C <sub>13</sub> -C <sub>25</sub> )	5	. 20	15	20	1
5	Mono- and Di- Cyclic Aromatics	2	5	15	15	0
6	$(C_6-C_{11})$ Polycyclic Aromatics $(C_{12}-C_{18})$	6	3	5	2	1
7	Naphtheno- Aromatics(C <sub>9</sub> -C <sub>25</sub> )	15	15	15	8	1
. 8	Residual	65	25			96
Estimated Maximum % Soluble		10	30	60	65	1
Estimated Maximum % Soluble Aromatic Derivatives		.1-10	.1-10	1-30	1-20	0-1
Reported % Soluble Aromatics Obtained In Seawater Extracts		.1 <sup>b</sup>	.01 <sup>a</sup> ,.1 <sup>b</sup>		.01 <sup>a</sup>	

# Table 5-4 Estimated % Composition (by weight) and Comparison of Solubilities For Various Petroleum Substances

proved bank agent asso

a. Boylan and Tripp (1971); Kuwait and kerosene extracts

b. Kuhnhold (1970); medium crude extract

c. Table values for BP 1002 would be similar to kerosene

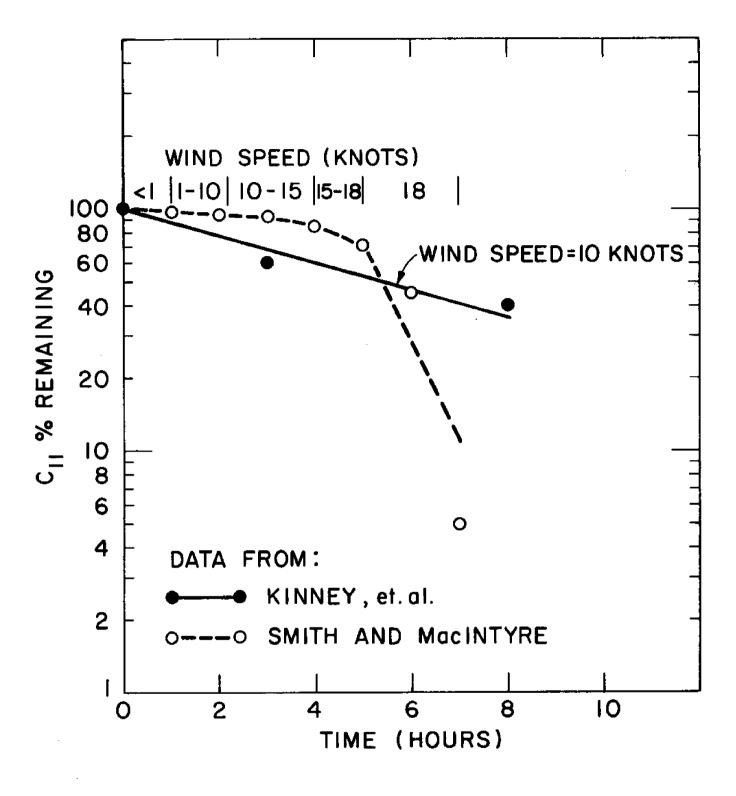
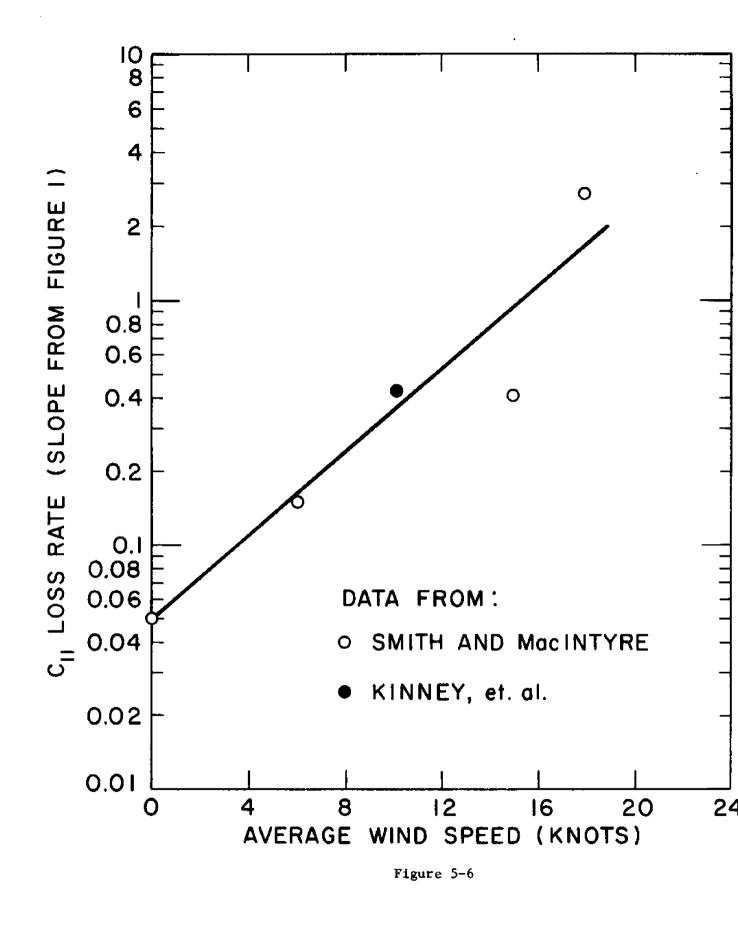
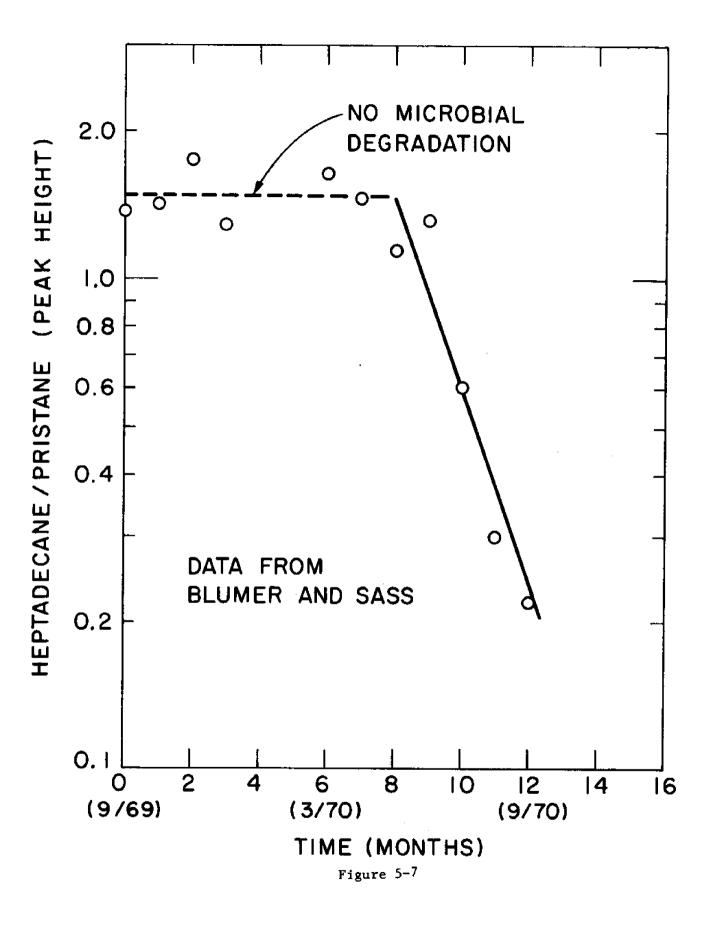


Figure 5-5

LOSS OF UNDECANE (C1) BY EVAPORATION AND DISSOLUTION



# EFFECT OF WIND SPEED ON WEATHERING



# MICROBIAL DEGRADATION OF HYDROCARBONS

#### 6. EFFECTS OF OIL ON MARINE ORGANISMS

6.1 Introduction

An examination of the effects of oil on biological systems must begin with a discussion of the influences of oil on individual organisms. Determination of effects on higher levels of the biological hierarchy (populations, etc.) are then possible, but more difficult. Section 6.1.1 establishes terminology and a general outline of oil effects on individuals and the transmission of the harmful effects of oil through higher biological levels (populations, communities, and ecosystems). Detailed assessments of the sensitivities to oil, and identification of critical concentrations for various marine organisms is included in Section 6.2.

6.1.1 A Framework

#### 6.1.1.1 Individuals

An individual organism is a complex structure consisting of many interconnected components: cells join together to form organs, which perform specialized functions; organs form less specialized systems; systems act together to maintain the whole organism. The first level at which a clear division is possible is the individual cell. The cell membrane serves as a highly selective barrier, allowing necessary substances into the cell, blocking out unwanted substances. It is an active process; the membrane uses energy to select between substances. Within the cell, specialized structures called organelles carry out the metabolic biochemical processes of the cell (e.g. respiration, photosynthesis, cell division). Enzymes play an essential role, speeding up biochemical reactions and allowing the cell to function. The direct contact of a harmful substance (e.g. a virus particle or oil) with an individual cell either kills the cell or is not harmful and the cell continues with its normal operations. Thus, at the level of each individual cell, the effects of a pollutant tend to be an "all or none" response.

Hydrocarbons may disrupt the cell in several ways including alteration of the cell membrane and the inhibiting of enzymes and other metabolically important molecules within the cell. Hydrocarbons are known to disrupt the lipid (fatty molecule) layer of the cell membrane, increasing its permeability (the ability for molecules to pass back and forth through the membrane) and causing death through the loss of vital cell components. Some organisms are able to resist the effect of crude oil because of their ability to metabolize (break down and oxidize) the hydrocarbons which enter the cells, and, in some cases, the ability of their cell membranes to resist the intrusion of hydrocarbons altogether.

In general, the low-boiling aromatic and aromatic derivative components of crude oil have proven to be the most toxic. However, low boiling straight chain (paraffins) hydrocarbons (10-12 carbons) may also cause a narcotic effect. In general, the water soluble (therefore, low boiling) fractions cause the toxic responses.

If cells are disrupted by oil, there is the possibility that the organs or organ systems which are composed of cells may also be disrupted. For the purposes of this study, any disruption at or below cellular level is defined as a <u>cellular effect</u>, while any disruption above the cellular level dealing with involuntary (biochemical) processes is defined as a <u>physiological effect</u>. Examples of physiological processes are blood circulation, secretion of digestive juices, and blood purification by filtration through the kidneys. Processes that are under instinctive and/or voluntary control are defined as behavioral. Examples are feeding and reproduction.

This categorization of oil effects is not always satisfactory. The death of cells may or may not disrupt organ functions which in turn may or may not alter the operation of the organ system, and so on. Each of these possibilities

depends on many factors, such as the composition and amount of oil, the sensitivities of the cell, organ and physiological system, the sensitivities of the cells in other physiological systems, and interactions among systems affected by the oil. Furthermore, cellular, physiological and behavioral effects are strongly linked. For example, if impulse transmission between cells in the nervous system is affected by oil, the behavior of the organism may be upset. Thus, the entry of oil into cells kills the organism or disrupts its behavior. A series of cascading effects in the individual organism leading from cellular through physiological to behavioral disruption undoubtedly exists for each organism that is sensitive to oil, the magnitude of the disruption being related to the particular organism's sensitivity to the oil.

In order to better describe the specific effects of oil on an individual organism five responses can be identified: 1) lethal toxicity; 2) sub-lethal disruption of physiological or behavioral activities; 3) the effects of direct coating by oil; 4) incorporation of hydrocarbons in organisms which cause tainting and/or accumulation of hydrocarbons in food chains; and 5) changes in biological habitats.

Lethal toxicity refers to the direct interference by hydrocarbons with cellular and sub-cellular processes, expecially membrane activities, leading to organism death. Sub-lethal disruption also refers to interference with cellular and physiological processes but does not include effects causing immediate death. The most important effects in this category are disruption of behavior, especially feeding and reproduction. The effects of direct coating do not result from biochemical interference of oil with cellular activities. The primary effects are smothering or mechanical interference with activities such as movement and feeding. The incorporation of hydrocarbons in organisms is of interest for two reasons: 1) because of potential accumulation of polycyclic aromatic

hydrocarbons (PAH), especially carcinogens, in various marine organisms; and 2) tainting of edible organisms with hydrocarbons. Habitat changes include effects from both oil spill and non-oil spill events. This group of effects consists of changes in the physical or chemical environment, which result in significant shifts in species composition and geographic distribution in the region of concern.

The relationship between cellular, physiological, and behavioral effects and toxicity, sublethal effects, coating, hydrocarbon incorporation and habitat changes are summarized in Table 6-1. Effects which alter behavioral patterns do not usually cause death directly, although an organism may be more susceptible to predation due to abnormal behavior. At the cellular level, hydrocarbons are usually either toxic to individual cells or have no direct effect at all. Weathered oil consists of high molecular weight hydrocarbons and is not transported into the cell, but may suffocate the organism by cutting off its source of oxygen. Habitat changes are usually caused by weathered oil which changes sediment textural characteristics.

#### 6.1.1.2 Higher Levels of Organization

The impact of oil at each successive level of biological organization (individual, population, community and ecosystem) is dependent on the impact at the previous level plus other variables unique to each level. Unfortunately the basic principles governing organization at each level are not that well understood (Section 3) and the ultimate assessments of impacts on an ecosystem are very difficult to quantify.

Most marine organisms are "r" strategists (Section 3.2.2): they lay millions of eggs in the hope that a few will survive to adult reproductive age. For most "r" strategists, the species population survives even if only a few adults survive and reproduce. Within a few generations, the population is able to return to normal size. However, if a stress is constantly present, the population may not recover.

Location of Action			
Effect	Cellular	Physiological	Behavioral
Lethal Toxicity	1	V	
Sublethal Effects		1	√
Coating With Weathered Oil		1	√
Incorporation of H.C.'s Into Food Webs	1	1	
Changes In Habitat		1	1

# Table 6-1 Important Possible Effects of Oil

Beyond the population level, any inference about the effects of oil on interactions between populations (i.e., a community) becomes difficult. Species interactions within a community form an exceedingly complex dynamic system. Even if the sizes of the different populations and their interactive links are known, it is seldom possible to predict the size of a given population at a given time. However, it may be possible to estimate the general trends that the community structure might follow, using simplifying assumptions about the community structure and the nature of the pollution. For example, Figure 3-5 schematically shows several different types of community structures arranged in trophic webs. Consider the trophic web captioned as "herbivore attacked by many species of parasites and predator". Under the toxic influence of oil, the number of individuals in the herbivore population could be greatly reduced. Because herbivores feed on plants and other animals feed on herbivores, the effects of oil could be serious for the other organisms, even though they are not directly affected. The plants having nothing around to eat them would overgrow the environment. The predators, on the other hand, would die off due to starvation.

Actually, no community is as well-defined as our hypothetical example. For example, pollock, herring, and mackerel eat their own and each other's eggs and larvae, as well as copepods. The fish larvae eat phytoplankton as well as each other. If this community was actually found in the sea, another herbivore, resistant to the concentration of oil which killed off the copepods, would probably migrate in, and would graze on the phytoplankton while serving as food for the carnivores at the same time. However, the structure of the community would be altered.

In any case, the impact on higher levels or organization is very dependent on the specific community structure of the area studied. Therefore, further discussion of these impacts is deferred to Section 8, in which the impacts of specific hypothetical events in the Machias Bay region are considered.

#### 6.1.2 Data Base

Before discussing the documented responses of organisms to oil, it is necessary to review the experimental procedures which provide the data base. Although a substantial number of studies have been carried out, investigating various biological aspects of oil pollution, there have been no comprehensive systematic studies of the whole problem as yet. In addition, there is a lack of standardization of the results of various studies. Accurate measurements have not been made of the concentration and composition of crude petroleum in solution, and the concentration and composition of fractions of petroleum in the bodies of animals and plants tested. Thus, in most cases, important pieces of information that provide the basis for comparison of different studies are missing. The complexity of petroleum substances amplifies this problem and makes it difficult to accurately analyze and specifically attribute biologically observed effects to even a limited fraction of the crude petroleum. Finally, a number of physical and biological processes significantly change the composition of crude petroleum over time, adding further difficulties. Despite these problems, there is enough information available to intelligently discuss various effects, the specific sensitivities of representative biological organisms, and draw some conclusions about the overall effects of crude petroleum and petroleum products.

Laboratory experiments are designed to examine the biological consequences of the <u>controlled</u> exposure of plants and animals to specific concentrations of pollutants. These experiments normally consist of a number of animals or plants of a particular species (e.g. fish, shellfish, algae) being placed in a large tank in which they are exposed to water or sea water containing petroleum components. The organisms are allowed to remain in the tank for varying periods of time (from minutes to hours), and then removed and, if still alive, may be placed in non-polluted water for varying periods.

Most studies evaluate the so-called <u>acute toxicity</u>, which is reported as the dose required to kill a specified percentage (usually 50%) of the test organisms during the exposure period. Various notations are used, such as  $\chi LC_y$ ,  $\chi LD_y$  or  $\chi TM_y$ , where  $\chi$  denotes the exposure period in hours and y denotes the percentage killed ( $\chi LD_y$  is used in this report). For example,  $8LD_{50}$  would be the dose required to kill 50 percent of the test organisms in 8 hours. In a few experiments, the organisms that survive the acute effects are observed for longer periods of time (days to weeks) and long-term toxicity and sub-lethal effects evaluated. Todd, et al. (1972) and Whittle and Blumer (1970) have reported the only extensive experiments which deal explicitly with the influence of sub-lethal concentration on behavior, survival, reproduction and community structure.

There are several severe limitations to the usefulness of experiments such as those described above. Most importantly, no standard experimental methods have been developed, especially with respect to petroleum fractions and media monitoring. The variability of composition, limited solubility and weathering of petroleum products require that the soluble fractions in the media be measured during the toxicity tests. However, this is almost never done. As a result, comparison of data is extremely difficult because different petroleum substances and different methods of addition (surface film, emulsion, etc.) are utilized in different experiments. Furthermore, the organisms are subjected to unnatural conditions and deprived of important interactions with other species and other normal environmental conditions.

Concentrations of hydrocarbons in the tissues of test organisms, before and after the exposure to oil, are rarely determined. The gas chromatography and spectroscopy equipment used in analyzing hydrocarbons is expensive and relatively complex, thus inhibiting widespread application to oil toxicity studies. Because these analytical techniques have not been extensively used

as yet, little data are available relating to background concentrations of hydrocarbons in the environment and in the tissues of individual species.

Even if hydrocarbon concentrations in animal tissues are measured after exposure, they are often reported in a form which makes comparisons with other studies difficult. Hydrocarbon concentrations are reported in the literature as grams per kilogram of dry weight tissue, or grams per kilogram of wet weight tissue, thus leaving to the reader the task of determining what percentage of the test organism is water. Frequently, the petroleum additive is described in the literature merely as "oil", "light crude oil", "mineral oil", etc., omitting the important information about composition especially soluble fractions.

Due to these shortcomings, the primary value of laboratory experiments is to establish order of magnitude boundary conditions on lethal toxicity. That is, concentrations of various substances can be identified which, if significantly exceeded, have a high probability of killing the organism of interest.

Only a limited number of experiments on plants and animals in the field have been undertaken. They consist of spraying or pouring crude oil, weathered crude oil, or petroleum products on specific areas in salt marshes or various coastal areas. Changes in fauna or flora are noted for various periods after their exposures. Spraying may be repeated at different time intervals over a period of months or years. The results are normally described as quantitative changes of numbers and density (number of organisms per unit area) of animals or plants present. In general, field experiments have the advantage of taking place in a "natural" habitat, thus allowing complex effects related to survival in an ecosystem to be evaluated. However, they are less quantitative and controlled. Frequently, the concentration of oil applied per unit area is not known precisely. In addition, although the experiments take place in a natural setting, they may be so restricted in size that significant effects are not

observed. A number of variables, such as predators, weather conditions, and physiochemical changes, cannot be controlled, and frequently are not noted in the literature. Major salinity changes because of runoff from heavy rains occurred in the Santa Barbara Channel at the same time as the oil spill. It is difficult to distinguish between deaths attributed to "natural" changes and those due to oil.

Extensive data is available from studies following actual accidental spills. Unfortunately prior examinations of the flora and fauna affected is usually not available. Typically these studies describe the organisms remaining and their recovery, but do not include estimates of the concentration of hydrocarbons to which the organisms were exposed. Often, dead organisms are counted, although only rarely are hydrocarbon concentrations in their tissues measured. The actual impact of a spill is highly dependent on weather conditions, time of year, local hydrography and physiography, and the area's previous history of oil spills. The length of time between release of the oil and its coming ashore are rarely directly stated in the literature. However, the extent of weathering that the slick has undergone can usually be ascertained by closely examining the description of the accident causing the spill which usually precedes discussion of biological effects in the article.

6.2 Effects of Oil on Individual Organisms

Assessments of the various effects of oil on individual organisms is summarized in the paragraphs below. For each of the five classifications of effects (see Section 6.1) data reported in the literature is summarized for several organism categories including: flora (phytoplankton, kelp, marsh grasses, etc.), pelagic fauna (finfish, crustaceans, larvae, etc.) and benthic fauna (molluscs, crustaceans, etc.)

#### 6.2.1 Lethal Toxicity

The data summaries for toxic responses (Tables 6-2 through 6-9) follow a standard format. For each organism or group of similar organisms the tables specify the common and scientific names, the type of experiment (laboratory, field or actual spill incident), the substance and amount used or spilled, an estimate of the actual amount of aromatic derivatives in solution, the test duration, the reported response, a reference citation and general remarks. Because toxic responses result almost exclusively from the soluble fractions of oil, it is important to determine the concentration of soluble hydrocarbons. In almost all reported cases this information is not provided. The estimates compare a variety of petroleum substances, and from the description of experimental methods given by the original authors. Soluble paraffin fractions are not included, because only the very low boiling fractions (Goldacre, 1968; Nelson-Smith, 1970) which would not be obtained under test or field conditions with petroleum mixtures.

### 6.2.1.1 Flora

Table 6-2 summarizes the toxic response of marine flora to hydrocarbons. Phytoplankton sensitivities vary over a wide range. A few species are apparently sensitive to concentrations of soluble aromatic derivatives (SAD) as low as 1 ppm. However, most species are unharmed by concentrations of 100 ppm or higher. Kelp are affected similarly. Note that Wilber (1968) reports no effects on kelp by the paraffin hexane (10 ppm), but significant effects of the aromatics benzene and toluene (10 ppm). Kelp and other macrophytes can be expected to be reasonably resistant due to excretion of mucous substances, which coat the stems and fronds of the plant, preventing damage. Most data for the response of marsh

grasses deals with effects of coating (Section 6.2.1.3). However, it is reasonable to assume that a toxic response to SAD concentrations of 10-100 ppm. Baker (in Cowell, 1971) provides a summary of the effects of oils on plant physiology. The long-term impact of spilled oils on plants depends on both toxic and coating effects, frequency of coating, and on the time of year.

#### 6.2.1.2 Pelagic Fauna

For the purposes of discussing oil effects on individuals, pelagic fauna are divided into finfish, larvae of all marine organisms (except those few with benthic larvae) and pelagic crustaceans. Data on finfish toxicity (Table 6-3) is not extensive and only a few species indigenous to the Gulf of Maine have been used in experiments. The data is not very conclusive, but an estimate of a toxic threshold of 5-50 ppm SAD seems reasonable, especially in light of the data reported by Wilber (1968). Because finfish avoid contaminated areas (Nelson-Smith, 1971)), there has not been a strong interest in the toxic response of these organisms.

The toxic effects of oil on larval stages of many marine organisms have been much more extensively studied (Table 6-4). Several investigators report that larvae appear to be 10-100 times more sensitive than adults (Mironov, 1968; Kuhmhold, 1970; Corner, et al, 1968). Typical concentration of SAD causing lethal toxicity are .1-1 ppm. However, at the lower concentrations death may be a delayed response. Typically the larvae may develop abnormally, leading to death several weeks after exposure. In a non-laboratory environment, such maldeveloped individuals are much more susceptible to predation, competition and other secondary effects. It is also interesting to note that larvae tend to be more sensitive than eggs. Apparently, this is due to the protection afforded the embryo by the chorion.

Table 6-5 summarizes the sparse data reported on the toxicity of pelagic crustaceans (shrimp and copepods). The critical concentrations may be

somewhat lower than those for fish and 1-10 ppm SAD is probably the lower threshold. Smith (1968) suggests that because of the small size (a few millimeters) of many pelagic crustaceans, toxicity may be a function of size. That is, the larger individuals are possibly more resistant.

6.2.1.3 Benthic Fauna

The benthic fauna are divided into four categories: gastropods (snails, limpets, etc.), bivalves (shellfish), crustaceans (shrimp, lobsters, etc.) and all others (worms, anemones, etc.). Apparently gastropods are the most resistant and crustaceans are the most sensitive.

Most gastropods studied (Table 6-6) indicate a rather high resistance to hydrocarbon toxicity and periwinkles (<u>Littorina littorea</u>), the common intertidal snail, is apparently very resistant. The critical concentration may be 100-200 ppm or more. Limpets (<u>Patella vulgata</u>) demonstrate the only significant deviation and appear to have a critical threshold concentration of less than 5 ppm. The relatively high resistance of gastropods may be due to secretion of a mucous substance (Shelton, 1971).

Bivalves, including oysters, clams, cockles and mussels are moderately resistant to oil (Table 6-7). The ability to close their shells and seal off the ambient water mass acts as an effective protection mechanism. However, this closed condition cannot be maintained indefinitely and, in fact, cockles tend to "gape" making them more susceptible (Simpson, 1968). Typical critical concentrations for most bivalves is 5-50 ppm SAD.

Both benthic crustaceans and other miscellaneous benthic organisms (Tables 6-8 and 6-9) are apparently fairly sensitive to SAD. Threshold concentrations appear to be 1-10 ppm of SAD. Burrowing organisms may also be threatened by alterations in the substrate texture and structure. However, these considerations are discussed in Section 6.2.5.

	244 7764			volstilization & bacterial degradation			auppression attributed to a decrease caused by oil	4 day LD <sub>50</sub> ≦? 650 ppm (our estimate from Kause data)	4 day LD <sub>5</sub> 0 ≜ 175 ppm (our setinate from Xance data)	4 day LD <sub>50</sub> <sup>22</sup> 70 ppm		
	REFRENCE	Kauns <u>et el</u> (1972)	-	÷	E	÷	I	Ĩ	z	=	E	
	RFSPONGE	growth suppressed	growth stimulated	no response	no response	growth inversely proportional to 7 saturation	growth suppressed	initial inhibition for 2 days, then growth lethal toxicity	slight inhib. lethal toxicity	slight inhib. lethal toxicity	2 day inhibition then stimulation	slight inhibition over 10 day period
	DURATION	117 days whole experiment	=		10 days	12 days	10 days	10 days 10 days 10 days	<u> </u>	10 dajve	10 da; m	10 daj s
	CARBONS IN SOLU- TION				1-5 ppm 1007 "saturation"	t	=	25-500 ppm 500-1744 ppm	25-250 ppm 500 ppm	25-50 ppm		
	SUBSTANCE AND REPORTED AMOUNT	M.S.O. crude 4.5 1/6 diam. test area (film on surface)	÷	Ŧ	Soluble extract From 50 ml in 1 liter water 0, 25, 19 50, 75, 100% "sat- uration"	5	Solulic extract from 50 ml "Culf" crude in one liter water 0, 10, 25, 50, 75, 90% "sat- uration"	Benzene	Tuluene	0-Kylene	7 Alberta crudes concentrations unknown	Smiley Colville (an Alberta crude) soluble extract
	EXPERDORT TYPE	FIELD (freshwater pond, June- October)	-	H	LABORATORY	ц	=	ŧ	-	-	÷	۲.
ORCANISM	SCIENTIFIC NAME	<u>Dinobryon</u> Sp. Sp. Sp.	<u>Tabellaria</u> Sp. <u>Ankistrodesmuy</u> <u>Bpiraies</u>	Frazillaría Sp. Ankístrodesmus falcatus	<u>Chlorococcum</u> Sp.	<u>Cosmarium</u> Sp.	Chlorella vulgaria	=	=	:	~	Chlorella vulgaris
Ċ	COMMON	Phyto- Plankton	=	5	:		=	:	T	F	:	Ŧ

TABLE 6-2 SUMMARY OF TOXIC RESPONSES FOR MARINE FLORA

			TABLE		IT RESPONSED	TABLE 6-2 SUMMARY OF TUALL RESERVISED FOR MARINE FLOW (CULL OF		
CORPON	ORGANISM SCIENTIFIC NAME	EXPERIMENT TYPE	SUBSTANCE AND REPORTED AMOUNT	ESTIMATED NYDRO- CARBONS IN SOLU- TION	DURATION	RESPONSE	REFERENCE	REVARKS
Phyto- Plankto	Numerous Species	Laboratory "	"oil" .00001-1.0 m1/1: most used .001-1. m1/1	(.01-1000. ppm)	5 days	death 1 m1/1. (1000 ppm) delayed cell division 1.0001 m1/1 (1001 ppm)	Mironov (1970)	does not describe oil used or whether concentrations quoted are soluble or not
Inter- tidal plants surf	<u>Phyllospadix</u> torreyii	incident v Santa Bar- h bara	veathered crude heavy coating		one tidal cycle	death through coat- ing & abrasion (smothering)	Foster <u>et al</u> (1971)	
Green algae (mid 6	Enteromorpha intestinalis	=	heavy coating various coatings			slight damage except where completely coated	ĩ	most intertidal algae have a mucous roar which aleds oil: high inter-
high inter- tidal	<u>Chaetceorpha</u> aerea	=	heavy coaling various coalings					tidal plants, where oil dried were damaged, season inportant1.e. blooms, subtidal plants not affected
	<u>ulva</u> scalifornica	2	heavy coating various coatings			U. californica re- covered in 4 months		
Bro⊌n aleae	<u>I.gregia</u> Javigata		various coatings			little damage	-	
Red Alcae	Porphyra sp.	=	z			killed-holds of I		
kelp	<u>Macrocystis</u> Ingustifolia	=	heavy coalifie			no damag <del>e.</del> mucous coat		
1	=	<u>rampico Maru</u> Laboratory	diesel fuel .01 <b>X-1</b> X emulsion	1-100 ppm	7 days	lo <b>ss</b> of photogynth. Bbillty	North <u>et al</u> (1964)	<u>Tampico Maru</u> spill resulted in kills to members all plyla.
Salt marsh grasses	Spartina Lownsendii	incidents: Milford Have & Torrey Canyon	fresh crude		20 min. after spill	75-1002 killed	Cowell (1971)	many other marsh plants studied but not summarized here
	Puccinellia Daritima	veathered crude (5 dispersants)			8 days			
Macro- phytic algae		lacident: Torrey Can- yon	weathered crude 6 dispersants			algae increased coverage of rocks	Bellamy <u>et al</u> (1967)	oil 6 diapersants killed herbivores, so algae overgrew rocks

6-2 SUMMARY OF TOXIC RESPONSED FOR MARINE FLORA (Cont. d)

	· · · · ·					
		Cysts (reprod cells) of these vere disrupted by oil, since they float near surface		brackish water species better able to withstand membrane damage caused by emulififer (sol'n in lipid layer)	germínation in annuals inhibited seasonally dependent	
		Kurtence Smith (1968)		=	Baker (1971)	Wilber (1968)
(D. 1001) WINTER ANY MANY AND ANY	43700328	lethal toxicity (reduced population)		generation time & lag phase lengthened below 1.2 ppm lethal toxicity at 1.2 ppm	sce p. 31 of Cowell annuals most suscep- tible, perennials most resistant	<pre>slight photosynth. Inhib. no effect visible injury, 75% reduction in photo-</pre>
	DURATION					96 hra. 96 hra. 96 hra.
	ESTIMATED HYDRO- CARBONS IN SOLU- TION			1.2x10 <sup>-3</sup> ppm 1.2 ppm		10 ppm 10 ppm 10 ppm
	SUBSTANCE AND Reported Anount	crude alick		BP 1002 emulsifier without kerosent	fresh crudes (Kuwait)	benzene n-hezane toluene
	EXPERIMENT TYPE	incident: Torrey Canyon		Laboratory	Field exper- iment (Milford Haven)	Laboratory
ORGANISM	SCIENTIFIC NAME	Phyto- <u>Prasinophyceae</u> planktoe <u>Halosphacra</u> sp.	<u>Pterosperma</u> sp.	various species Laboratory	various species Field exper- fresh crud. iment (Kuwait) (Milford Haven)	<u>Macrocystic</u> angustif <u>olla</u>
	C OMMON NAME	Phyto- plankto		÷	Salt Darch grasses	Kelp

TABLE 6-2 SUMMARY OF TOXIC RESPONSES FOR MARINE FLORA (Cont'd)

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FINFISH
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RESPONSES
TOXIC
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SUMMARY
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TABLE

	ORGANISH			ESTIMATED HYDRO-	-			
COMMON	SCIENTIFIC NAME	EXPERIMENT TYPE	SUBSTANCE AND REPORTED AMOUNT	CARBONS IN SOLU- TION	DURATION	RESPONSE	REFERENCE	REMARKS
Atlantic Salmon	Salmo salar	Laboratory	Corexit 8666 1-19.000 mg/l complete emulsion		7-14 days	4 day LD <sub>50</sub> >10,000 mg/l	Sprague & Carson (1970)	authors point out probability of sublethal-long-term effects of oil dispersant at lower conc.
£	Ĩ	z	1-10,000 mg/l complete emulsion BP110C B BP1100 Gulf arent 1009 Nanhtla gas Dispersont 88' Dispersont 88' Dispersont 88' XZIT x-1-11	2-200 ppm	7-14 days	4 day LD <sub>50</sub> 1-100 mg/1		authors believe Corexit is microbially degraded; the by- products of this process, either from Corexit or Waste from microbes, are toxic after 7 day's building in test tank
=	z	Ŧ	1-10,000 mg/l terporary emulaton Bunker C	0-1 ppm	7-14 days	4 day 1D 210,000 mg/1 7 day 1D <sub>50</sub> ~2000 mg/1		
z	¥.	-	Bunker C & Corexic 8666		7-14 days	4 day]1.D50 7 day ≃100-1000 ±g/1		
Flounder (vinter)	Pseudopleuro- Nectes Americanus	5			7-14 days	4 day LD <sub>50</sub> >10,000 mg/l 7 day LD <sub>50</sub> ° 1000 mg/l		
íresh water fish	<u>Mucil saliens</u> Sargus annulari: Crenilabrus Lenca	1	"oil" .25 ml/l		"many days" "several days"	no effect	Mironov (1970)	emulsion more toxic than film
r'laice	Rhombus maeoticus	=	"o11" 10 <sup>-4</sup> -10 <sup>-5</sup> m1/1		2- days	lethal toxidity to even	=	
bitat	Alnsa sapidisuima	5	Gasoline #2 Diesel fuel Bunker C			LD50 24 48 96 Gas 91 91 - #2 204 167 - C -2,417 1,952	Tagatz (196 )	loss of texicity by evaporation
fullet	Mugil cephalus Micropuson undulatus	Ξ	#2 Diesel off .01-10% emuisified	mqq 2-200.		LD <sub>50</sub> (48 hrs.) ~420 ppm (acute) LD <sub>50</sub> (chronic) 42 ppm	Texas In- struments (1971)	safe at 4.2 ppm

							-	
DRGANISM			. — 1	ESTIMATED HYDRO- (				
COMONN NAME	SCIENTIFIC NAME	EXPERIMENT TYPE	REPORTED AMOUNT	CARBONS IN SOLU- TION	DURATION	RESPONSE	REFERENCE	REMARKS
Roach	Rut <u>tius</u> sp.	Laboratory	cyclohexane benzene methylcyclohexa	10 ppm 10 ppm ne 10 ppm	3-4 hrs.	lethal toxicity Relgon-Smith (1970)	ethal toxicity Nelson-Smith (1970)	
Sunflah		5	Phenanthrene Naphthalene Xylene, toluene benzene, ethyle	4-5 ppm 4-5 ppm e 22-65 ppm ene	1 hr,	lethal toxicity wilber (1968)	Wilber (1968)	
Thread herring	Ophistonema onglinum	incident: Ocean Eagle Sán Juan	crude oil ƙ emulsifiers			95% of schools Cerame Vivas near spill had (1968) lestons	Cerame-Vivas (1968)	

TABLE 6-3 SUPPARY OF TOXIC RESPONSES OF FINTISH (Cont.'d)

<b>*</b> -9	
TABLE	

1	,,		1			<del></del>	·	
	REMARKS	no information on experimental methods	Ē	1		-	Libyan (high paraffin content) did not cause increases in mortality; 10 day old larvae less sensitive	Young larvae less resistant than embryo; Herring less resistant; Plaice more re- sistant; Libyan crude affected larvae more than embryos
	REFERENCE	Mironov (1968)	, ,	James (1926) reported in Kuhnhoid (1970)	Mironov (1967) reported in Kuhnhold (1970)	Kuhnhold (1969) reported in Kuhnhold (1970)	Кићпћо1d (1970)	£
F MARINE ORGANISMS	RESPONSE	40 to 100% hatched prelarvae perished	Larvae 100 times more sensitive than aduits	35% pulled in stagnant vater, not affected in running water	100% eggs killed	100% eggs killed	40% Migher mortal- 1ty than control 10-20% increase in mortality 99% killed 63% killed 33% killed 21% killed 21% killed	Lime to deach for Larvae exposed for 1 day
AND EGGS O	DURATION			96 hours	2-3 days	2.5-3.5 days	100 hours	1-10 days 4.2 days 8.4 days 14 days 14 days 3 to 6 hours no effect
TOXIC EFFECTS OF OILS ON LARVAE AND EGGS OF MARINE OFGANISMS	ESTIMATED HYDRO- CARBONS IN SOLU- TION			07	.01 - 1 ppm		.loppa andqi. .naqqi .uopa .uoqt.	l0ppm lppm .lppm control 100-1000 ppm
SUMMARY OF TOXIC RFFECT	SUBSTANCE AND REPORTED AMOUNT	"oil" 10 <sup>-4</sup> -10 <sup>-5</sup> ml/1		Bunker C film - 100 ppm	10-100 ppm dis- persion of Russian crude	10 <sup>3</sup> and 2x10 <sup>4</sup> ppm film	cxtract of Vene- zuelan oil in water 10 <sup>4</sup> ppm extracts of Iranian crude 10 <sup>4</sup> ppm 10 <sup>3</sup> ppm 10 <sup>3</sup> ppm control	uxtracts of Tranian crude in water 10 <sup>4</sup> ppm 10 <sup>3</sup> ppm 10 <sup>2</sup> ppm 10 <sup>2</sup> ppm 10 <sup>3</sup> plus 10-100ppm 00rrexit 7664 10-100ppm Correxit
SUM	EXPER IMENT TYPE	Laboratory		Laboratory	Laboratory	Laboratory	Laboratory	Laboratory
	ORGANISM SCIENTIFIC NAME	<u>Rhombus</u> maeot1cug	Balanus sp.				<u>Gadus</u> Borrhua	<u>oerthua</u> morthua
	COMMON	<b>Plaice</b>	Barnacle	Cod and Flounder	Black Sea Turbot	llerring	po	Cod

TABLE 6-4 SUMMART OF TOXIC EFFECTS OF OILS MN LARVAE AND FEGS OF MARINE ORGANISAS (Cont'd)

		considerable ty delayed and	much more and other a to 100		:t; .1 ml/l	sitive	rosene	aitive	
	REMARKS	set original article for considerable more detail; some mortality delayed due to effects on feeding and larval develorment	original article contains much more data on other dispersants and other tests; adults resistant up to 100 ppm BP1002		.001 m1/l had little effect; .1 m1/l very toxic	Urching generally very sensitive	death definitely due to kerosene solvent in <b>E</b> P1002	Larvae 10-100 times as sensitive as aduirs	
	REFERENCE	W11400 (0261)	Corner, <u>et al</u> (1968)	Smith (1968)	Welle (1972)	Allen (1971	Wilson (1968)	Portmann 4 Connor (1968)	
(P)	RESPONSE	<pre>10 ppm BP1002 killed 100%; 2.5 ppm BP1002 reduced survival by 50%</pre>	0 - 3 ppm BP1002 increase mortality some reduction of activity	50-90% of eggs in plankton tows dead	24-96 hrs. 96LD <sub>50</sub> = .03 - 002 ml/l	fertilization mot affected; lowest dilutions interfere with fertilized egg development	Ippm caused 100% mortality; .5ppm caused abnormal development	lppm BP1002 lethel	
VISKS (Cont	DURATION	1-30 days	varloue		24-96 hrs.		several hours to several days		
AND FEES OF MARINE ORGANISES (Cont'd)	ARBONS IN SOLU- ARBONS IN SOLU-	0 – 2 ppm	0 - 20 ppm 1 ppm		(mdd 1-10°)	(mq 1-1.)	.12 ppm	.2 - 2 ppm	
	SUBSTANCE AND REPORTED AMOUNT	0 - 10 ppm BP1002	0 - 100 ppm BF1002 1000 ppm Kuwait	Kuwait and emulsifiers	.0011 ml/l Venezuelan crude	extracts of 25ml crude and bunker C oils in 500ml eea water 5.257 - 507 dilucions	.5 - 1 pp: 871002	1 - 10 ppm BP1002	
	EXPERIMENT TYPE	Laboratory	Laboratory	Torrey Canyon Incident	Laboratory	us Laboratory	Laboratory	Laboratory	T above to
ORCANISM	SCIENTIFIC NAME	<u>Pleuronectas</u> <u>platessa</u>	<u>Bodestus</u>	<u>Sardine</u> píkhardug	<u>Homarus</u> americanus	<u>Strongylocentrorus</u> purpuratus	e <u>Sabellaria</u> <u>spinulosa</u>	ns geveral	(reserves
ð	COMMON	Piatce	Barnacle	Pilchard	Lobsters	Sea Urchin	Polychae ce	Crustaceans	(teres

5
CRUSTACEAN
PELACITS
40
40 STIO 01
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RESPONSES
TOXIC
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SIMMARY
6-5
TABLE

SCIENTIFIC     EXPONSE     CLABBONS IN SOLU- NAME     DUMATION     RESPONSE       NAME     TTPE     REPONTED ACOUNT     TION     RESPONSE       Several species     Laboratory     .001-1     mL/l     (possiby)     .001 mL/l     100 mL/l       Several species     Laboratory     .001-1     mL/l     (possiby)     .001 mL/l     .001 mL/l     .001       Penacue sp.     Laboratory     .011 mL/l     (possiby)     .01-100 ppm)     .001 mL/l     .001 mL/l     .001       Penacue sp.     Laboratory     .012 ppm)     (1-100 ppt)     .010 mL-l     .011 mL/l     .001 mL/l     .001       Penacue sp.     Laboratory     Crude oil plus     (1-100 ppt)     .010 mL-l     .011 mL/l     .001       Palasmonetes sp.     Laboratory     Laboratory     Laboratory     .2-10 ppm     1 hour-3 days     .50 pm detregent       Calanus     Laboratory     Laboratory     L-50 ppm     .2-10 ppm     1 hour-3 days     .50 pm detregent       Calanus     Remotetes sp.     RP Laboratory     Laboratory     Laboratory     .2-10 ppm     .2-10 ppm       Calanus     RP Laboratory     Laboratory     L-50 ppm     .2-10 ppm     .2-10 ppm     .2-10 ppm       Calanus     RP Laboratory     Laboratory     L-50	ORCANISM				ESTIMATED HYDRO-				
It letter       Laboratory       .001-1. mi/l       L-100 ppm)       Lond ppm       Insensitive to death with .1         Pennetus sp.       Laboratory       .011 vill       L-100 ppm       001 mi/l, 100X       001 mi/l, 100X         Pennetus sp.       Laboratory       crude oil plus       (1-100 ppt)       01 mi/l       100X         Palaemonetes ap.       Laboratory       trade oil plus       (1-100 ppt)       00 mi/l       100X         Palaemonetes ap.       Laboratory       Laboratory       1-50 ppm       1.200 ppm       000 mi/l       000 mi/l         I       Calmus       Laboratory       Laboratory       1-50 ppm       1.2-10 ppm       1.1000 mi/l       000 mi/l       0000 mi/l       000 mi/l<	CONHON XANE	SCIENTIFIC NAME	EXPERIMENT TYPE	SUBSTANCE & REPORTED AMOUNT	CARBONS IN SOLU- TION	DURATION	RESPONSE	REFERENCE	REMARKS
Penaeue sp.Laboratorycrude oil plus(1-100 ppm)(48LD50 = 1-40 ppcPalaemonetes ap.(1-100 ppt)(1-100 ppt)crude oilcrude plus CorexitPalaemonetes ap.(1-100 ppt)(1-100 ppt)crude plus CorexitPalaemonetes ap.(1-100 ppt)(1-100 ppt)ppm detergentPalaemonetes ap.(1-100 ppt)(1-100 ppt)ppm detergentPanaetin(1-100 ppt)(1-100 ppt)(1-100 ppt)Panaetin(1-100 ppt)(1-100 ppt)(1-100 ppt)Panaetin(1-100 ppt)(1-100 ppt)(1-100 ppt)Panaetin(1-100 ppt)(1-20 ppt)(1-100 ppt)Panaetin(1-20 ppt)(1-20 ppt)(1-100 ppt)Panaetin(1-20 ppt)(1-20 ppt)(1-100 ppt)Panaetin(1-20 ppt)(1-20 ppt)(1-20 ppt)Panaetin(1-20 ppt)(1-20 ppt)(1-20 ppt)Panaetin(1-20 ppt)(1-20 ppt)(1-20 ppt)Panaetin(1-20 ppt)<	Copepod	Several species	Laboratory	.0011 m1/1 "120"	(possibly 1-100 ppm)		fnsensitive to .001 ml/1, 100% death with .1 ml/1	Mironov(1969), cited in Mironov (1970)	experimental methods not described
Palaemonetes     sp.       Palaemonetes     sp.       Falaemonetes     sp.       Calamus     Laboratory       Laboratory     1-50 ppm       Finmarchicus     S0 pm       Gamen     .2-10 ppm       Finmarchicus     S0 pm       Gamen     .2-10 ppm       Finmarchicus     S0 pm       Gamen     .2-10 ppm       Calamus     .2-10 ppm       Finmarchicus     S0 pm       Gamen     .2-10 ppm       Dasic     Canten       Moughton Solvent     tality in an hour       Moughton     10-1000 minutes       Masic     tality in an hour       Dasic     tality in an hour       Pandalus     tality in an hour       Dasic	Shrimp	Penaeus sp.	Laboratory	crude oil plus emulsifiers (1-100 ppt)	(I-100 ppm)	-	48LD <sub>50</sub> = 1-40 ppt crude of1	Mills and Culley (1971)	see reference for detailed breakdown; oils with higher propor- tion of aromatics most toxic
CalanusLaboratory1-50 ppm.2-10 ppm1 hour-3 days50 ppm detergentfinmerchicumsEP 1002.2-10 ppmcaused 1007 mor- tality in an houriCamtenCamtenCamten5-10 ppm detergentCamtenCamtenCamten5-10 ppm detergentCamtenCamtenSolventgents caused highMoughton Solvent112Popm112Acartia clausiLaboratory5-100 ppmppmAcartia clausiLaboratory5-100 ppm1-20 ppmBP 10021-20 ppm10-1000 minutes1ethally toxicPandelusLaboratoryBP 100248 hr. LDtrationsPandelusLaboratoryBP10025.8 ppmconnor (1968)		<u>Palaemonetes</u> sp.					481D <sub>50</sub> = .5-5 ppt crude plus Corexit		
Acertie clausi Laboratory 5-100 pm 1-20 ppm 10-1000 minutes BP 1002 Dasic Pandalus Laboratory BP1002 <b>*</b> 48 hr. LD <sub>50</sub> = Montagui 5.8 ppm	Co pe pod	<u>Calanus</u> <u>finnerchicus</u>	Laboratory	1-50 ppm BP 1002 Camlen Dasic Molyslip Houghton Solvent 112	.2-10 ppm	1 hour-3 days	50 ppm detergent caused 100% mor- tality in an hour 5-10 ppm deter- gents caused high mortality in a days; 1 ppm was injurious	Smith (1968)	
Pandalus Laboratory BP1002 - 48 hr. LD <sub>50</sub> - 5.8 ppm 5.8 ppm	Copepod	<u>Acartia clausi</u>	Laboratory	5-100 ppm BP 1002 Dasic	1-20 ррт	10-1000 minutes	lethally toxic at all concen- trations	Ŧ	BP 1002 5 times as toxic as Dasic; <u>Acartia</u> much less resistant than <u>Calanus</u> ; suggests small animals toxicity is related to size
	Pink Shrim		Laboratory	BP1002		48 hr. LD <sub>50</sub> = 5.8 ppm	Portmann and Connor (1968)		

NO BO				TOUTOWN IN CHEWN 10W IT WITH A LINE ALL AND THE ALL AN	TA MERICAN TONY	TAN TOUT OWN		
NKGA NKGA	ORGANISH			ESTTMATED HYDRO-				
CONTION	SCIENTIFIC	EXPERIMENT 5	SUBSTANCE &		NUTTON	RESPONSE	"EFERENCE	R EMARICS
Dog Whelk	Vucelle lapidus	Incident	"dispersants"		     	stance taceans	Shelton (1971)	Gastropods can produce copious mocus secretion
Perfulnkle	Littorina littorea							
Pertwinkle	Littorina littorea	Incident: <u>Arrow</u>	Bunker C			ingestion of oil Scarratt no effect (1970)	Scarratt <u>et al</u> (1970)	intertidal contact with oil- oil passed through digestive system nummodified - nn untere in other
Periwinkle	Littorina <u>littorea</u>		fresh crude oil			sensitive"	Nelson-Smith (1967)	organs
Limpets	<u>Acmea</u> sp.	Incident: <u>Santa</u> Barbara	weathered crude oil	heavy coat		little damsge	Foster, et al (1971)	limpets appeared to be feeding on oil
Perivinkla Limpet Dogwheik	Littorima neritoides Littorima Baxatiliis Patella Vulgata Umbilitoalis Cibbula Littorina Obtusata	Field	Kuwait crude (fresh) Kuwait crude (weathered) DP 1002 (single in DP 1002 (single in comgination) v2 liters/m		5 min 6 hours	general relative ( toxicity to gaatro poda BP 1002 > fresh>> weathered	Crapp in Cowell (1971)	data difficult to summarize by species; experiments were amall scale and contained many uncon- trolled variables, making quanti- fication of results difficult
same 6 spectes as above as above		Laboratory	BF 1002 BF 1002			toxicity dependent on season: least toxic in winter (water temp. 10°C) highest in summer (water temp. 18°C) BP 1002 much more toxic than BP 1100	Ŧ	saue comments as above
Limpet <u>7.</u> Perlwinkle <u>1</u> Periwinkl, <u>1</u> }	Patella vulgata Littorina Littorea Littorea Littoralis	aboratory	varioua crudes		sprayed on for 1 hr. then vashed	<pre>1-89% mortality for treasy in 1.11ttoralis L. cowell (1971) 11ttorea very resistant. P. vulgata very sensitive</pre>	ttuway in Sowell (1971)	high mortality correlates with asphaltenes & low boiling com- pounds (aromatica, cspecially).

-6 SUMMARY OF TOXIC RESPONSES OF CAST

TABLE 6-6 SUMMARY OF TOXIC RESPONSES OF CASTROPODS

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	REWARKS	intertidal species periwinkles may recover from 100 ppm all detach from substrate before dying	data supports Ottway's conclusions	oil weathered for 24h in lab. simulated tidal washing in lab.
	REFERENCE	Smith (1968)	Ferkins in Carthy 5 Arthur (1968)	
	ISKOASI	LD <sub>50</sub> ∧ 100 рр <b>ж</b> LD <sub>50</sub> ∧ 100 ррж LD <sub>50</sub> ≈ 100 ррж LD <sub>50</sub> ≈ 5 ррж	96h LD <sub>50</sub> = 5 ppm 2 24h LD <sub>50</sub> = 250 ppm 24h LD <sub>50</sub> = 2000 ppm	weathered oil les toxic than oil å BP 1002
	DURATION	24 hrs. "		
(cont.)	ESTIMATED HYDRO- CARBONS IN SOLU-	0-20 ppm	0-400 ppm	
	SUBSTANCE 6	T	BF 1002 0-200 ppm BF 1002	crude oil weather ing BP 1002
	EXPERIMENT	a Laboratory	Laboratory 'Laboratory	=
	SCIENTIFIC	vit Art Art Art Art Art Art Art Art Art Ar	Limpet <u>Patelle vulgata</u> Laboratory Periwimkle <u>Littorina litto</u> r <sup>4</sup> Laboratory Periwimkle 1. <u>littorea</u>	Perivinkle <u>1</u> . <u>littorea</u>
	NSIN NO	Periwinkle Dog Whelk Top-shell Limpet	Limpet Perfufnkle Perfufnkle	Periwinkle

			48LD <sub>50</sub> for man detergents given	incorpotation of Bunker C after Arrow Spill			Also obtained information on sublethal concentrations		subtidal speciel				simulated tidal conditions
(HS)		REFERENCE	Portmann & Connor (1968)	Scarrat, <u>et al</u> (1970)	Perkins (1968)	Perkins (1968)	Sm1th (1968)		=		S impson (1968)	Neigon-Smith in Repple (1971)	
SUMARY OF TOXIC EFFECTS OF OIL ON MARINE BIVALES (SHELLFISH)		RESPONSE	481.0 <sub>50</sub> for	011 content 100-125 ug/gm	24LD <sub>50</sub> = 90ppm 48LD <sub>50</sub> = 2ppm	24LD <sub>50</sub> = 20ppm	5ppm BP1002 not lethal in 24 hours; l0ppm BP1002 lethal	no deaths, but mussels could not attach properly	24 hre. LD <sub>50</sub> =0.5pp	24 hrs. LD <sub>50</sub> =1ppm	10-100ppm BP1002 lethal	481D <sub>50</sub> = 500ppm	no taxicity for crude oil only; 502 mortality with Dispersol plum oil
F CIL ON MAR		DURATION	variable				24 hours						4 tidel cycles
OF TOXIC EFFECTS OF C	Damkn GalfAlltsa	CARBONS IN SOLU- TION	0-20 ppm		v. 4ppm	v. 4 ppm	0-20 ppm	ne da par			~2-20ppm		
SUMMARY C		SUBSTANCE & REPORTED AMOUNT	detergents	Bunker C	B71002	BP1002	5	1000ppm crude emulsion	BP1002		BP1002	phenol	"laboratory" weathered (24 hours) Aratian crude plus Correxit or Disper- sol app;oximately 5m1/m <sup>2</sup> + 107 dispersant
		EXPERIMENT TYPE	Laboratory	Field (Arrow Spill)	Laboratory	Laboratory	Leboratory		Laboratory		Laboratory		Laboratory
	ORGANISH	SCIENTIFIC NAME	<u>Cardiun</u> <u>edule</u>	<u>Modiolus</u> modiolus	<u>Mycflus</u> edulis	<u>Cardium</u> edule	<u>Myrtlue</u> edulis		Ensis siligua	Chlamys Opercularis		<u>Cardlum</u> edule	<u>Yytilus</u> edul <u>is</u>
	c	COMMON	Cockles	Mussel	Mussel	Cockle	Mussel		Razor claa	Queen scallop	Oysters	Cockles	Xuesle

86

TABLE 6-7

TABLE 6-7 SUMMARY OF TOXIC REPECTS OF OIL ON MARINE BIVALVES (SHELLFISH) (Cont'd)

			,				-	
-	ORGANISM			ESTIMATED HYDRO-				
COMMON	SCIENTIFIC NAME	EXPERIMENT TYPE	SUBSTANCE & C REPORTED AMOUNT	CARBONS IN SOLU- TION	DURATION	RESPONSE	REFERENCE	REMARKS
Mussels	Hussels <u>Mytilus</u>	Laboratory		0-100ppm	34 days	10 <sup>4</sup> and 10 <sup>5</sup> ppm	Danter,	individual from srea (Coal Point)
	<u>californianus</u>		Santa Barbara			caused significant Straughan,	Straughan,	subject to natural seeps possibly
			crude ( as surface film)			mortality	and Jessee (1971)	less susceptible than those from other areas; data not conclusive
Mussels	Mussels rivtilus	Laboratory	1000mg/1 mineral	0	up to 6	no mortality	Lee (1972)	primarily an experiment to
	edulis		oil (paraffin only)		daya			investigate uptake and incorpora-
			1-8mg/1 heptadecane	0	up to 6	up to 6 no mortality		tion
			100ppm tetralin	loopa	up to 6	texic		
			lppm loluene.	lppm	upyeo 6	not toxic		
			napthalene,		days			
-4			3,4-benzpyrene					

		REMARKS						lobster fishery of Chedabucto Bay not damaged by Arrow spill; lobsters considered very resistant						
		REFERENCE	Portmann k Connor (1968)			Corner, <u>et al</u> (1968)		Scarratt <u>et al</u> (1970)	Perkins (1968) in Carthy 6 Arthur (1968)			Smith (1968)	· · · · · · · · · · · · · · · · · · ·	
SN1		RESPONSE	48LD <sub>50</sub> for BF1002=5.8ppm	BP1002 48LD <sub>50</sub> -15pp=	вр1002 241.0 <sub>50</sub> =20рр <b>н</b>	100% mortality with 100ppm; 5ppm shows sub lethal effect	some inhibition of cirral beat	4 day LD <sub>50</sub> for Bunker C > 10,000 ppm	100% survival at 10ppm	96 hours LD <sub>50</sub> = Sppm	96 LD <sub>50</sub> = 30ppm	241.D <sub>50</sub> = 10pp <b>e</b>	24LD <sub>50</sub> = 2ppm	24LD <sub>50</sub> = 25ppm
RIC CRUSTACE		DURATION	48 hours	48 hours	48 hours	48 hours	24 hours	7-14 days						
MARINE BENTHIC CRUSTACEANS	ESTIMATED HYDRO-	CARBONS IN SOLU- TION	s tlppm	radd €.^	∿4 ppen	020pp#	.lppm		2 ppm	1.ppm	6 ppm	Zppm	4ppm	ζppm
		SUBSTANCE 4 REPORTED AMOUNT	various emulsifiers	various emulsifiers	various caulsifiers	1-100ppm BP1002	100ppm film of Kuvait	Bunker C <sup>f</sup> and various dispersent	BP 1002	BP 1002	5P 1002	BP 1002	ъ <b>Р</b> 1002	BP 1002
		EXPERIMENT TYPE	Laboratory	Laboratory	z	÷		z	=	*	-	=	Ŧ	:
	ORGANISM	SCIENTIFIC NAME	<u>Crangon</u> crangon	<u>Carcinus</u> maenas	<u>Homarus</u> gamarus	Elminius modestus		<u>Homarus</u> americanus	<u>Balanoids</u> balanoids	Eupagurus bernhardus	<u>Carcinus</u> maenas	<u>Cancer</u> pagures	<u>Crangon</u> vulgaris	<u>Carcinus</u> macnas
		COMMON NAME	Shrimp	Shore crab	Lobster	Barnac les		Lobsters	Barnacles	Kermit Crab	Crab	Crab	Shrimp	

TABLE 6-8 SUMMARY OF TOXIC EFFECTS OF OIL ON MARINE BENTHIC CRUSTACEANS

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TABLE 6-8 SUMMARY OF TOXIC EFFECTS OF OIL ON MARINE BENTILC CRUSTACEARS (CON

				MARINE BENTH	MARINE BENTHIC CRUSTACEANS (CONT'D)	KS (CONT'D)		
HO	ORGANIŚM			ESTIMATED HYDRO-				
CONTION	SCIENTIFIC NAME	EXPERINGNT TYPE	SUBSTANCE & REPORTED ANOUNT	CARBONS IN SOLU- TIONS	DURATION	RESPONSE	REFERENCE	
H <b>ermit</b> Crab	<u>Díogenes</u> pu <u>gilator</u>	Laboratory	BP 1002	Sppm		24LD <sub>50</sub> = 25ppm	Smith (1968)	
Barnacle	Barnacle <u>Balanus</u> <u>balanoides</u>	z	crude o11	2 pọm		2% is toxic	Nelson~Smith in Hepple (1971)	
many species		Field	Kuwait BP 1002				Crapp in Cowell (1971)	many field experiments and data which is difficult to summarize; data indicates little toxic response of most species to weathered kuwdit.

	SXIVIAL									only code names of 10 dispersants are given. Sandworm is one of most		Mucus secretions of worms and in- ability of oil to penetrate mud may have prevented toxicity	oil may have been dispersed into mud by emulsifier and ingested by		crude oil concentrations given were not completely dissolved
	REFERENCE	Perkins in Carthy & Arthur (1968)	Smith (1968)	Perkins in Carthy & Arthur (1968)	Smith (1968)	÷	Ŧ	Nelson-Smith in Hepple (1971)	Smith (1968)	LaRoche <u>et al</u> (1970)		George (1970)	=	00 00	100.000 
VERTEBRATES	RESPONSE	96 hr. LD <sub>5</sub> 0 - 30ppm	24 hr. LD <sub>5</sub> 0 - 25ppm	24 hr. 1,050 - 40 ppm 96 hr. L050 - 30 ppm	24 hr. LD <sub>50</sub> - 25-50ppm	24 hr. LD <sub>50</sub> = 25 ppm	24 hr. LD <sub>50</sub> - 5ppm	"quickly lethel"	24 hr. LD <sub>50</sub> = 25	96 hr. LD 50 - 165ppm 50	96 hr LD <sub>50</sub> = 6100ppm	little damage	high mortality	24 hr. LD <sub>5D</sub> () Essolvene 63	162 Larmful at 10 00 ppm (not cecessar[]y co lately in so fon) dispersion ore toxic the
OTHER BENTHIC INVERTEBRATES	DURATION													비원	
	ESTIMATED HYDRO- CARBONS IN SOLU- TION	p ppm	ang č	6-8 ppm	510 pres	5 ppm	1 ppm		udd s		0				
	SUBSTANCE & Reported amount	BP 1002	BP 1002	BF 1002	Ŧ	=		crude 0.1-5%	BP 1002	"BP"	"crude oil B"	fresh fuel oil coating on mud surface	fuel oll § Essolvene	BP 1002 Essolvene Corexit 7664	Corexit (0-500 ppm) ppm (elick) & mixtures
	EXPERIMENT TYPE	Ľ	=	Ξ	÷	I	=	=	:	=	Ŧ	Incident: shore ter- minsi spill	=	Laboratory	Laboratory
	SČIENTIFIC NAVE	<u>Arenícola marína</u>	<u>Nereis</u> diversicolor	<u>Asteriae rubens</u>	2 species	<u>Å. rubens</u>	Ophiccomina nigra	e <u>Tubularía</u> <u>crocea</u>	Calliactig parasitica	<u>Nereis virens</u>	Ŧ	Cirriformia tentaculata	=	-	several species
	ORGANISH COMMON VAYE	Polychaete annelid	Ξ	s tarf 1sh	Ane mones	starfish	Brittlestar	Coclenterate <u>Tubularia</u> <u>crocea</u>	-	Sandworm	Ŧ	Polychaete annelida	=	-	Coral

TABLE 6-9. SUMMARY OF TOXIC EFFECTS DF OIL OW OTHER BENTHIC INVERTEBRATES

#### 6.2.1.4 Summary of Toxicity Data

Table 6-10 summarizes the review of toxicity data. For each group of organisms the estimated range of critical concentrations for various petroleum substances are shown. The estimates of #2 Fuel 0il and Fresh Crude are based on information summarized in Table 5-4.

#### 6.2.2 Sub-Lethal Effects on Behavior

Most marine organisms depend upon a complex set of behavioral characteristics to maintain a normal life pattern. Many of these behavioral patterns, especially feeding and reproduction, involve communication based on chemical clues called pheromones. Chemical communication has been extensively studied in insects, but only recently has significant attention been given to marine animals. However, sufficient information is available to draw tentative conclusions regarding the possible effects of oil on chemical communication.

Early studies by several investigators (see Hasler, 1970 ) focused on migration habits and territory recognition by fish, especially salmon. More recent work has focused on feeding, reproduction and social behavior in fish and lobsters (Todd, et al., 1972). In addition, Whittle and Blumer (1970) have investigated the role of pheromones in predation by starfish. Extrapolation of the results of these laboratory experiments to natural environments is extremely difficult (probably more so than toxicity tests). The objective of the experiments is to assess behavioral characteristics, however, the organisms are placed in very "unnatural" environments<sup>1</sup>, which likely disrupt behavior in themselves. In addition, the chemical clues are apparently extremely subtle and occur in very low concentrations, which makes actual identification difficult. Introduction of foreign substances may in fact block these communication signals, but

<sup>&</sup>lt;sup>1</sup>Todd, et al. (1972) have attempted to alleviate some of these problems by using large aquariums and several species of organisms simultaneously.

		ted Typical Toxicity R	anges (ppm) fo	or Various Substances
Class or Organisms	SAD <sup>1</sup>	#2 Fuel Oil/Kerosene	Fresh Crude	Weathered Crude
Flora	10-100	50-500	10 <sup>4</sup> - 10 <sup>5</sup>	Coating More Signifi cant than Toxicity
Finfish	5-50	25-250	u	
Larvae	.1-1.	. 5–5	$10^2 - 10^3$	· · ·
Pelagic Crustaceans	1-10	5-50	$10^3 - 10^4$	
Castropods	10-100	50-500	$10^4 - 10^5$	· · · · · · · · · · · · · · · · · · ·
Bivalves	5-50	25-250	TI.	1
Benthic Crustacaens	1-10	5-50	$10^3 - 10^4$	
Other Benthic Invertebrates	1-10	5-50	$10^3 - 10^4$	

## TABLE 6-10 Summary of Toxicity Data

1 - Soluble aromatic derivatives (aromatics and napthenoaromatics)

the foreign chemicals may also induce other behavioral responses, only indirectly disrupting normal communications.

The most remarkable part of the utilization of pheromones is that they are recognized at extremely low concentrations. Whittle and Blumer (1970) found starfish react to oyster extracts in concentrations of parts per billion. Sea lamprey can respond to specific chemicals (amines) at 20 parts per billion, hydra and coelenterates respond to glutathione at 30 ppb, and eels recognize  $\beta$ -phenylethyl alcohol at concentrations on the order of molecules. Clearly some marine animals have extremely sensitive olfactory and taste organs. More remarkable is the specificity of the animal's response, being able to differentiate among a myriad of compounds in sea water. The apparent reliance on the ability to differentiate between chemical clues raises serious questions about the effect of blocking of the chemical receptions, the masking of chemical clues, and the substitution of "false" chemical clues.

One of the most significant set of studies has been carried out by Todd, et al. (1972), examining the bullhead fish which has an extremely complex set of social behaviors. The bullhead is capable of differentiating between species and can even recognize individual fish - making paring relationships possible. Many fish which live in schools have no individual relationships or social structure. The Bullhead lives in communal life with clear social functions among dominant and subordinate individuals. (Todd attributes this highly complex behavior to subtle chemical clues.)

Todd has found that the bullhead brain has enlarged olfactory (smell) lobes and performs a highly integrative function for the senses. Other fish have less developed olfactory areas, and less complex behavior. He concludes that complex behavior is related to a highly developed capability of smell; taste is basically utilized for feeding function. To test this hypothesis the olfactory

and the taste organs were destroyed and the bullhead's behavior analyzed. The results show that the bullhead suffered marked loss of the capability of social behavior (mates were attacked and unrecognized) when the olfactory area was destroyed. This indicates significant dependence on chemical clues to maintain complex behavior.

In experiments with lobsters, Todd found that lobsters were attracted and then repulsed by soluble aromatic components of kerosene but that straight chained paraffins had no noticeable influence. Kerosene and the branched and cyclic paraffins induced searching and feeding behavior. Kerosene, polar aromatics, and branched cyclic fractions also initiated agitated grooming behavior. Conceivably,lobsters could be attracted to an oil spill because of the polar aromatic component and the other components of crude oil could disrupt social organization and individual behavior patterns, or even cause lethal or sub-lethal effects from exposure.

Todd has postulated an inverse relationship between physiological toughness and behavioral complexity, i.e. the more complex the behavior patterns for a fish,the lower the adaptability (resistance) to stress (pollution). The most complex behavioral species will have difficulty producing highly resistant strains in a stressed area, i.e. the adaptation of these species will take place but not as successfully as species with simpler (less complex) behavior patterns. Moreover, Todd expresses the proposition that there is a relationship between increased behavioral complexity and ecological complexity. The most complex behavioral species appear in the most stable, mature, i.e. diverse, ecosystem. Therefore he postulates the vulnerability of an ecosystem to stress is related to behavioral complexity, i.e. there is increased vulnerability of an ecosystem with increasing numbers of behaviorally complex species which can only appear in mature ecosystems.

The validity of these conclusions is uncertain without more data. It is evident that individual species dependent upon many chemical clues to maintain complex behavior are particularly vulnerable (if Todd's experiments can be generalized), but there is no indication that they are less able to adapt over time to environmental changes than less behaviorally complex species. In fact, population and community level survival may be enhanced due to behavioral complexity. A mature ecosystem typically contains behaviorally complex species which is usually more diverse and stable. Thus, while it may contain a larger number of individually vulnerable species, the mature ecosystem, because of its diversity of animals and plants, should be better able to absorb stress than less mature, i.e., less diverse systems.

In reviewing the field of chemical communication in marine organisms, and assessing their vulnerability to crude oil a few conclusions can be drawn. However, they must be tempered with the realization that the field is not extensively developed and most of the experiments are preliminary. Field conditions may considerably alter behavioral responses and circumstances of exposure, thus either enhancing or diminishing effects while revealing new problems. Moreover, higher boiling hydrocarbons have not been used in any experiments, and it is this portion of crude oil that is the long term contaminant of the environment.

Apparently, disruption can occur from relatively low concentrations of petroleum substances (10-100 ppb). However, the toxic properties of the low boiling component may be more important than the chemical communication disruption. More importantly it is unclear whether the behavioral changes that might occur can lead to permanent damage to individuals and populations.

The extent of chemical communications in marine animals is substantial and plays an essential role in behavior. Although the present evidence for the effects of crude petroleum on chemical communication is limited, the problem in terms of long term effects related to successful adaptation or survival could be serious. Any introduction of large quantities of hundreds of chemical compounds should be a cause for concern, requiring both accelerated experimentation examining possible consequences and a sense of caution in decision-making regarding any new possible modes of release into the marine environment.

#### 6.2.3 Incorporation of Hydrocarbons

The most important effect of oil on marine organisms from the point of view of public health is the incorporation of hydrocarbons in food chains. There is ample evidence that a variety of marine organisms do, in fact, incorporate and accumulate hydrocarbons (Blumer, 1970; Lee, 1972; Zobell, 1971). Incorporation of hydrocarbons themselves apparently does not effect the organisms directly. However, two problems are important to man: 1) accumulation in organisms of polycyclic aromatic hydrocarbons, especially carcinogens; and 2) tainting of edible species.

The introduction and dispersal of carcinogenic compounds into the environment has been of increasing general concern over the last few decades. Besides the increase of lung cancer related to air pollution and smoking, there has been a steady rise in many types of cancer in the U.S. and other industrialized countries. While much of the increase can be attributed to successful prevention and treatment of other formerly fatal diseases - influenza, typhoid, tuberculosis - and the consequent increase in life span and the older population, part is related to increasing environmental contaminants from a number of sources - automobiles, industrial waste, food additives, etc.

Crude petroleum and its fractions contain hundreds of compounds, most of which are not carcinogenic. However, petroleum also contains polycyclic aromatic hydrocarbons (PAH) and other individual compounds, some of which are proven carcinogens.

6.2.3.1 Cancer and Polycyclic Aromatic Hydrocarbon Compounds

Polycyclic Aromatic Hydrocarbons (PAH) are multi-ring aromatic compounds. The most carcinogenically active compounds are found in substituted tri (3) and tetra (4) cyclic aromatic hydrocarbons. Some penta (5), hexa (6), and higher cyclic compounds are also included. PAH were identified as the active carcinogens in petroleum and coal products and residues, e.g. petroleum asphalt, coal tar, soot, lubricating oils, which caused increased incidents of skin cancer in exposed workpeople. It was found that oil containing more than 0.03% polycyclic aromatic hydrocarbon (PAH) with 4 or more rings caused cancer. (Gerarde, 1960)

The carcinogenic properties of polycyclic aromatic hydrocarbons are attributed in part to the presence of certain chemical structures in the compound. The mode of action appears to be chemical rather than physical and may relate to the properties of hydroxylyzed metabolites (compounds formed from the original compound) or mutagenic (mutation-causing ability) properties of carcinogens or their metabolites to disrupt cellular growth. Given the specific properties needed for carcinogenic activity, it is important to ascertain whether these compounds are changed in the food chain, and if they are, into what products.

PAH carcinogens occur naturally in a variety of plants, and are distributed throughout the food chain. Fresh water algae have been found to synthesize a variety of PAH carcinogenic compounds. Algae <u>Chlorella vulgaris</u>, which synthesizes several PAH's, was found to contain 10-50 µg/kg (dry weight)

of PAH compounds. Apparently PAH carcinogens are growth stimulants in plants, and their carcinogenic potency appears to be related to their growth stimulating power. PAH have been found to increase 10-100 fold after germination in higher plants. In phytoplankton, production of aliphatic and aromatic hydrocarbons including carcinogenic PAH's, may be as much as three tons per year per square kilometer. Anaerobic bacteria synthesize appreciable quantities of hydrocarbons including 3, 4-benzpyrene, 1, 2-benzathrene, 3, 4- and 10-benzfluoranthene. Specifically the bacteria <u>Clostridium putride</u> assimilates lipids of dead plankton and forms 120 to 800 ug benzpyrene (BP) per kilogram of plankton material (dry weight). Thus a large number of "natural" sources of carcinogenic compounds exist, confusing the distinction between "natural" or contaminated areas.

The wide distribution resulting from natural and man-made sources is illustrated by benzpyrene (BP), an extensively studied carcinogen (Zobell (1971)). BP has been found in marine sediments, fish, shellfish, and plankton in both contaminated (Europe and American) and uncontaminated (Greenland) Blumer found 40-1300  $\mu$ g/kg BP in soil that he considered uncontamiareas. nated. Table 6-11 shows the range of concentrations of BP for a variety of marine animals, plants and sediments, and other categories. The uncontaminated general level of food is put at  $10-20 \ \mu g$  of BP per kilogram (dry weight). Although most concentrations of BP in the environment are low, contamination of sediment can reach 5ppm, and in marine animals about 1/10that level. From Table 6-11 the presence of BP in the sediment and marine flora and fauna in the same area is indicated, thus demonstrating that contamination of the sediment may lead to contamination of marine organisms. However, significant concentrations are also found in organisms from uncontaminated areas such as the coast of Greenland. In discussing the distribution

Kind of animals	Geographic location	BaP, μg/kg
Oysters	Norfolk, Virginia	10 to 20
<b>"</b>	French coast	1 to 70
Mussels	Toulon Roads, France	2 to 30
Holothurians	· Villefranche Bay, France	up to 2000
**	West coast of Greenland	กปี
Codfish and shellfish	12 19 25 33	16 to 60
Fish nad shellfish	Saint-Malo Bay, France	3 to 125
Fish and crustaceans	Villefranche Bay, France	nil to 400
Crustaceans	Arctic Ocean	nil to 230
Isopod crustaceans	Clipperton Lagoon	up to 530
Various fishes	Adriatic Coast, Italy	nil to 900
Invertebrates	19 29 19	nil to 2200
Material	Geographic location	BaP , µg/kg
Mud (42 stations)	Tyrrhenian Sea	1 to 3000
Mud from pyster beds	French coast	90 to 2840
Mud (17 stations)	Mediterranean coast	up to 1800
Mud (8 stations)	Villefranche Bay, France	16 to 5000
Mud (12 stations)	French coast	nil to 1700
Mud and sand	Villefranche Bay, France	nil to 1700
Calcareous deposits	Franch coast	8 to 59
Surface mud	Italian coast	nil to 2500
Mud (218 samples)	Adriatic coast	nil to 3400

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Table 6-11 Quantities of 3,4-benzpyrene Detected in Marine Animals and in Bottom Deposits. (Zobell,1971)

of BP in the environment, it should be remembered that it constitutes only a variable protion of the total PAH present, perhaps 1-20%. Therefore, low concentrations of BP are deceptive if they are interpreted to indicate low accumulations of PAH without other confirming analysis.

There are a number of general sources of PAH hydrocarbons including oil spills, coal tar, petroleum asphalt, and cooking oil. Crude petroleum has been found to contain a number of carcinogenic PAH compounds including 1, 2benzanthrene, chrysene, triphenylene, 1, 2-benzphenanthrene, phenanthrene, and dibenzthiophene. Various crudes have been analyzed for their content of BP and a range of values from less than 0.1 ppm to more than 1 ppm has been found. Naphthenic and asphalt-based petroleum contain more quantities of carcinogenic PAH's than paraffin-based crudes because the greatest proportion of those crudes are made up of high molecular weight hydrocarbons. It should be noted that the relative proportion of carcinogens per kilogram of crude will increase after weathering removes low boiling fractions. Zobell (1971) estimates that a spill of 10,000 tons of oil could contain 100-200 lbs. of carcinogenic material.

PAH compounds are very insoluble. Their solubility is increased by the presence of detergents or non-colloidal hydrocarbons (purines, acetone) but the concentrations of the detergents needed to achieve these increases are unrealistic especially in marine environment. Therefore the primary mode of distribution of PAH hydrocarbons is adsorption (adherence) onto particulate matter.

The clearest evidence for the absorption of PAH compunds if from a study by Lee et al. (1972). They found that the marine mussel <u>Mytilus</u> edulis incorporated a number of hydrocarbons including 3, 4-benzpyrene. However,

most of the compounds remained in the gut, indicating a lack of absorption in the body. BP is excreted, but some remains even after removal from the source of contamination. Apparently, unlike mammals and bacteria, no substantial degradation of PAH compounds takes place in mussels, copepods and fish once absorbed into the tissue. This poses the problem of accumulation of PAH carcinogens even if little is absorbed at one time through the digestive system. Thus crude petroleum spilled into the environment, even if only slightly soluble, or carried on particulate matter, might accumulate in edible fish and shell fish. However, Lee, et al. (1972) indicates that there may be a maximum accumulation concentration in mussels.

The oxidation of BP and other PAH carcinogens occurs in the presence of sunlight. However, degradation is slower in oil than in aqueous solution. Therefore much of the PAH compounds will be protected from easy oxidation, and this process is likely to be comparatively slow. Another route is degradation by bacteria from water and soil. The lack of nutrients, especially phosphorous and nitrogen compounds, may reduce the extent of degradation. Finally, some animals metabolize carcinogenic hydrocarbons, but marine organisms in general do not seem to possess this ability.

The clearest indication of the length of time necessary for effective degradation comes from the work of Blumer et al. (1972), on stranded crude oil. The reduction of various types of compounds in oil over a period of years was examined. Only slight degradation of PAH compounds occurred. Though theoretically it is possible to oxidize and microbially degrade the PAH compounds in crude oil, two factors cause the half-life of the compounds to be in years. First is the preference of bacteria to degrade n-paraffins, branched paraffins, and cycloparaffins before they attack PAH compounds. The second is that despite the considerable ability of bacteria

to rapidly degrade these compounds, optimum environmental conditions rarely exist to allow these rates to be attained.

In summary, PAH carcinogens tend to remain in the environment capable of being adsorbed on particulate matter or absorbed by burrowing animals, and thus provide routes to enter the food chain. Edible fish and shellfish can partially absorb these compounds through their gut tract. Marine animals do not appear to metabolize them to a significant degree when they enter their tissues. Potentially slow accumulation can occur; moreover, ample evidence is available to show this process does indeed occur for a number of fish and shellfish.

Although man does not absorb PAH to any substantial extent through the gastrointestinal tract (Gerarde, 1960), even a small absorption of these compounds into the body or incorporation in the gastrointestinal tract presents a danger of inducing cancer, especially in light of the medical judgement that prolonged low level exposure to carcinogens can be the most effective way of producing cancer. Although the human body does metabolize these compounds, initially by hydroxylation, it is still uncertain whether the metabolites are themselves carcinogenic. Thus an increase in exposure would constitute an increased health danger.

#### 6.2.3.2 Tainting

Tainting of marine organisms also results from incorporation of hydrocarbons. However, rather than only PAH's causing the problem, all fractions, especially soluble low boiling fractions, may cause tainting. Numerous investigators have reported data relating to tainting (Blumer and Sass, 1970; Lee et al. 1972; Mackin, 1961; Nelson-Smith, 1971; Tarzwell, 1971; Wilder, 1970; and Sidhu, et al. 1970).

Filter feeding organisms, especially bivalves and some finfish, such as mullet, are particularly susceptible to tainting. Nelson-Smith (1971) reports that concentrations in water as low as .01 ppm of crude oil cause tainting in oysters. Experiments by Wilder (1970) indicate that lobsters become tainted only by immersion in sea water containing oil, but not from eating oil coated food. This is particularly significant, because it indicates that incorporation of hydrocarbons in the food chain may result from direct removal from sea water and not from feeding and ingestion of food containing petroleum substances. Burns and Teal (1971) report that #2 fuel oil spilled in a salt marsh was incorporated by nearly all the organisms in the marsh ecosystem.

The concentration threshold for the development of objectionable taste in animal tissue is in the range of 5-50 ppm (McKee and Wolf (1963)). However, gas chromatography (Blumer, 1970) is capable of detecting concentrations at much lower values (ppb range). Data from Lee et al. (1972) indicate that for various types of hydrocarbons there may be maximum amounts that will be incorporated by a particular organism. For the mussel <u>Mytilus edulis</u> he found that aromatic hydrocarbon concentration in the organisms may reach 70 ppm (dry weight basis). Blumer and Sass (1970) reported concentrations of hydrocarbons from 5-70 ppm (wet weight) in various shellfish heavily contaminated by a #2 fuel oil spill. The data from Lee also indicate the efficiency with which filter feeders remove hydrocarbons from sea water. Significant levels of hydrocarbons could be detected in the organisms within 2-4 hours after placement of mussels in contaminated seawater.

A simple example can illustrate the sensitivity of filter feeders to very low concentrations of hydrocarbons in water and the potential problems that can result. Chipman and Galtsoff (1949) have reported that oysters

filter 200-300 liters of water/day. Assuming a wet weight of 5 grams and a taste threshold of 50 ppm ( $\mu$ g/gm), a simple computation shows that exposure to as little as 1 ppb hydrocarbons in water for one day can lead to significant contamination:

$$\frac{50 \ \mu g}{gm} \cdot \frac{5 \ gm}{organism} \cdot \frac{1}{200 \ 1/day/organism} = 1.25 \ ppb/day$$

Organisms contaminated with oil do have some capacity for self-cleaning. (Mackin, 1961; Lee et al., 1972; Blumer and Sass, 1970). Apparently, the longer and heavier is the exposure, the more persistent is the tainting. In short term experiments, Lee found that the mussel, <u>Mytilus edulis</u> discharged more than 90% of the incorporated hydrocarbons after being placed in clean water. However, Blumer and Sass (1970) report much less self-cleaning in organisms exposed to contaminated sediments over longer time periods.

In summary, tainting is a significant sub-lethal problem. Very low concentrations in water (1-10 ppb) are of importance and can lead to tainting of organisms in very short time periods.

## 6.2.4 Effects of Coating

This section is intended to deal exclusively with the problems associated with coating by a film of oil. This is only of importance when the oil has been weathered, so that the more toxic (at the cellular level) fractions have evaporated. If the toxic fractions are present, the damage done by coating is insignificant compared to the damage done at the cellular level by the low boiling aromatic oil fractions. Most of the data dealing with oil coating discusses the damage done by an oil slick that had weathered at sea for several days before coming ashore (for example, see Chan, 1972).

The organisms most endangered by coating are those which are not able to leave the area where weathered oil is emulsified in the water column, or

has settled on the bottom. This immediately excludes from further discussion finfish and other mobile pelagic organisms which can recognize the presence of oil at low concentrations in seawater and presumably avoid higher concentrations. Birds and marine mammals present a different problem since they may not recognize an oil slick until coating is inevitable.

The distinction between the physical effects of a coat of oil on an organism and the effects of the hydrocarbon components of the oil on the physiology of the organism must be repeated here. Toxicity refers to the effects of one or more hydrocarbon fractions which disrupt the cellular or subcellular functions of the organism, so as to cause death if the disruption is widespread and severe enough. This implies that hydrocarbons come into contact with the cell membrane, and either pass within the cell to disrupt metabolic processes, or disrupt the function of the membrane itself. Coating causes disruption of the system or organism level. For example, a coat of weathered oil covering the respiratory apparatus of an organism will not harm individual cells by contact, but will kill the organism by depriving all its cells of oxygen. Death in this case is not a function of the fractions which are harmful at the cellular level); the same effect could probably be induced by using the same volume of Elmer's glue.

In terms of respiration and feeding interference when considering littoral or benthic organisms, a division can be made by differentiating between sessile and mobile organisms. Whether or not an organism can move away from oil deposited on the bottom plays a large role in determining whether it survives or not. Even if an organism is sessile and becomes covered with oil, it still may be able to protect itself (e.g. bivalves) until the oil is removed or until the oil layer becomes shallow enough for

the organism to break through to clean water. (Remember, the cellular toxicities of the hydrocarbons present in the layer are assumed insignificant.) Chan (1972) found that mussels could poke through a weathered oil slick that coated them after the San Francisco spill with only a 3% mortality.

In many filter-feeding organisms, the feeding and respiratory organs are closely coupled, so that interference with one will almost inevitably affect the other. Good examples of these organisms are most molluscs (bivalves like clams and snails) and crustaceans (barnacles, some types of small shrimp, etc.). Many shellfish filter water through their gills and strain the suspended material they do not want with out everything, surround mucus and eject it, eating the rest. At the same time, they receive oxygen from the water passing over the gills. If oil is emulsified in the water, the droplets will be strained out also. As long as the amount of oil is small (a few percent of the total water volume being filtered) the organism should be able to surround the oil in mucus and eject it. A heavier emulsion will probably suffocate the organism. Also, the amount of dissolved oxygen per unit volume in the water fraction of the emulsion may decrease as the amount of oil increases because the oil may be oxidized naturally at a slow rate, using up dissolved oxygen. This could cause suffocation also. It is quite difficult to quantify the amount and composition of oil, length of exposure, extent of emulsification and amount of dissolved oxygen present to obtain an estimate of the susceptibility of organisms to coating. Also, it is difficult to generalize for even small taxonomic groups of organisms, since very wide ranges in response to oil are sometimes found among organisms even within the same genus (the level of classification just above the species).

Movement and attachment to a substrate are also influenced by the presence of a coat of oil, but these are discussed in the section on habitat changes.

If coated for a prolonged period, macrophytic algae ("seaweeds") may show a decrease in photosynthesis due to decrease in incident light penetration and a lack of  $CO_2$ . Oil droplets may adsorb on the surfaces of phytoplankton, but because of the short cell division times of most singlecelled phytoplankton the population is not likely to be effected. Again, these effects are difficult to quantify.

Zooplankton, which are capable only of small scale active movement (they can move over long distances by drifting with oceanic currents), may be subjected to oil-water emulsions in a manner similar to that encountered by benthic organisms. Most zooplankton are crustaceans, but many have filterfeeding mechanisms similar to those of bivalves (see Yonge (1928) for a good summary of the many types of feeding mechanisms employed by invertebrates). This would make these organisms susceptible to coating by an oil-water emulsion. Plankton are commonly found in the surface layers of coastal waters. Because the oil-water emulsion is formed by wind and wave action at the surface, filter-feeding plankton may be subjected to more concentrated emulsions than would be expected in deeper waters. The literature on coating of plankton by oil is sparse and is summarized in a review by Nelson-Smith (1970).

Straughan (1971) investigated the effects of the Santa Barbara spill on several species of marine mammals which inhabit the area, but could come to no conclusions. These mammals must periodically surface in order to receive air, and thus are in danger of being coated with oil. One dead dolphin found washed ashore in Santa Barbara reportedly had its blowhole

plugged with oil, although this finding has been disputed (Straughan, 1971).

Many weaned elephant seal pups were coated with oil and were apparently not harmed, although immediate mortality could have been much higher had the oil spill taken place at a time when the pups were feeding. Odell (in Straughan, 1971) reported a tripling in the number of premature births of sea lions, which, like the sea elephants, have rookeries on the islands in the Santa Barbara Channel.

It seems probable that marine mammal mortalities can only be indirectly related to coating. Warm blooded marine organisms must maintain their body temperatures at a higher level than the surrounding water. This requires an efficient insulating layer surrounding the body. Birds use a layer of waterproofed feathers, while mammals usually combine layers of fat with a thick coat of fur as insulation. A coat of oil can significantly change the insulating properties of the fur, perhaps causing the animal to lose heat and lower its resistance to disease. This is just one of several possible hypotheses that can be used to indirectly connect oil coating with marine mammal mortality, although based on current evidence, none of these hypotheses can be accepted conclusively.

Birds are also warm-blooded and thus must insulate themselves against their surroundings. Marine birds have an additional problem because their insulation must also be waterproof. Straughan (1971) summarizes the effects of coating of birds with oil. Aerial species rarely come into contact with oil, whether floating or beached, and thus are not especially endangered. Swimming species are continually subject to contact with floating oil slicks. Often their first reaction upon coming in contact with the oil is to dive beneath it invariably resurfacing in it, compounding the problem. The oil

causes the insulating layer of feathers to mat down, causing the animal to freeze, or die of a disease caused by loss of metabolic heat. The buoyancy maintained by the air-filled feathers is also disturbed. Feeding may become difficult, both because the bird may experience difficulty in movement, and because food sources may be contaminated by oil (Nelson-Smith, 1970). 6.2.5 Habitat Changes Induced by Spilled Oil

One major problem connected with oil activity is the incorporation of oil into sediments. The amount of crude oil and the percentage of different fractions which compose it in the sediments are functions of: a) the particle size distribution of the sediments, b) the strength of vertical mixing, c) the water depth, d) the time after the spill and the extent of its weathering. The amount of vertical mixing and water depth determine whether or not the oil will reach the bottom by means of forces. Vertical mixing is dependent on the surface winds, the extent of stratification, and current mixing. Also, the density of the oil in the slick is a function of the extent of weathering, because lighter components are lost, making the oil more dense as time progresses.

Once mixed in the water column, oil is usually adsorbed onto the surfaces of any particles suspended in it, generally settling to the bottom after a time. The amount of oil adsorbed by the sediments correlates with particle surface area. On a unit mass basis, it is known that the smaller the sediment particles are, the more total surface area there is. Thus, all other things being equal, there will be more oil in clay sediments than in sandy sediments.

Once incorporated in the sediments, the oil tends to degrade slowly. At the surface of the sediments, aerobic (oxygen-utilizing) bacteria can degrade some fractions of the oil, but beneath the aerobic layer, anaerobic

(oxygen-free) conditions frequently prevail, which do not allow microbial degradation. Oil in this state is frequently present for months or years before it breaks down, assuming no new oil is introduced in the meantime.

As discussed in Section 4, the size of the sediment particles play a major role in determining which organisms live in the sediments. Obviously, the presence of oil will have some effect. Detritus feeders such as many gastropods tend to live in finer sediments (silt and clay). These animals swallow the sediment whole and digest any bacteria and organic matter, excreting the remainder. Filter feeders inhabit coarser sediments (sand and gravel). For detritus feeders, oil in the sediments presents an obvious danger. Absorption of hydrocarbons through the digestive tract is serious, as is the possible destruction of food sources by the oil.

Another problem caused by oil may be either a retardation or acceleration of natural sediment drift rates, which determine the stability of the substratum. This is especially important in coastal areas, where estuaries could silt in, or salt marshes could erode away, their stabilizing grasses having been destroyed.

#### 6.3 Summary

In the preceding sections the biological effects of oil on individual organisms have been reviewed. Several important considerations are apparent from this review:

1. As many authors have noted, the aromatic fractions of oil pose the most serious environmental problems. Although low molecular weight (10 carbons or less) alkanes can cause narcosis, the concentrations required to induce such responses are extremely high and would not occur from an oil spill.

2. Concentrations of water-soluble aromatic derivatives (aromatic and naphtheno-aromatics) as low as .1 ppm may be toxic to larvae of most marine organisms.

3. Most adult marine organisms are sensitive to soluble aromatic derivatives in concentrations of 1 ppm and lethal toxicity typically occurs at concentrations of 10-100 ppm. In general, crustaceans and burrowing animals are most sensitive, fish and bivalves moderately sensitive and gastropods and flora least sensitive. However, fish and other mobile organisms are generally known to avoid and escape contaminated areas.

4. Chemical communications play an important role in the behavioral patterns of many marine organisms. The full implications of disruption of these communication patterns remain uncertain, as does the exact mechanisms of disruption. However, concentrations of soluble aromatic derivatives in the range of 10-100 ppb may cause significant rpoblems.

5. The incorporation of hydrocarbons in the tissue of marine organisms is primarily of interest due to public health. The individual organisms are apparently not affected. Whether or not cancer can be induced in humans from ingestion of carcinogens accumulated in seafood is as yet unknown. However, the potential seriousness of the problem implies that careful consideration be given to these issues. The actual mechanisms of build-up in the food chain also remain uncertain. There is some evidence that incorporation results primarily from uptake directly from sea water and not from ingestion of contaminated food sources. In addition, there is a general, slow degradation of hydrocarbons, indicating that the ultimate fate (after many years) may be stable, innocuous compounds.

6. The development of objectionable taste in seafood (10-50 ppm in the organism) can result from very low ambient concentrations in water (1-10 ppb) of hydrocarbons in a relatively short amount of time (one to a few days). If the contamination in the water is short-lived and concentrations in water are not too high, self-cleaning of the organism may be 90% complete. However,

the maintenance of undesirable water conditions over longer time periods can result in essentially permanent contamination of the organism.

7. The effects of weathered oil are coating, usually in the intertidal zone, of both organisms and substrates. If coating is heavy, the effects may be essentially permanent, due to smothering of individuals

or alteration of substrate textures. Light coating of weathered oil is not, in general, a major problem. Frequency of coating is also important and areas subject to chronic discharge may accumulate the oil, leading to longer term problems.

The conclusions outlined above provide the basis for assessing the possible impacts of various hypothetical events relating to oil supertankers. Spill probabilities and trajectories can be used to estimate where and when various hydrocarbon fraction concentrations can be expected. Using this information the impacts on specific organisms can be estimated. The ultimate impact, however, is the effect on communities and the ecosystem. These assessments are best made in the context of specific locations, organisms, and events and are therefore considered in Section 8.

Finally, little has been said to this point about non-oil spill related events. In particular, problems associated with construction and tanker operation are of interest. The background necessary for assessing these effects, however, is not extensive and these impacts are also reviewed in the context of specific events in Section 8.

## 7. POTENTIAL SPILL TRAJECTORIES AND BEHAVIOR<sup>1</sup>

## 7.1 Introduction

A spill can be transported many miles through the action of the wind and current, as well as through its own tendency to spread. Regions of high spill probability are therefore not only local problems, but also an "upstream" source of oil that will affect places many miles away. The prediction of what is upstream and what is downstream in the flat,windblown expanses of the ocean requires an understanding of how the wind, waves and current work to push a slick around. The spreading of the oil is also important, because the areal extent of a slick will dictate the width of the path that the oil will sweep, and subsequently how much oil will be deposited on a given length of shore.

7.2 Basic Model

#### 7.2.1 Mechanics Governing Spreading

Spills can occur in two fashions. They can be the result of some nearly instantaneous release, such as the rupture of a tank, or they can be the result of a long-lasting, continuous release, such as that which occurred in the Santa Barbara oil spill. The distinction is based on the time scales involved, which in turn are dictated by the volume and character of the oil as well as the physical dimensions of the spill region. The physics governing the spread of the oil is of course the same, but subtle differences will exist in the time dependency. For the purposes of this study it is sufficient to examine just the instantaneous type it is the simpler of the two.

Consider now a volume of oil suddenly dropped on the surface of the sea. Presume that there are no restraints on the boundaries of the oil

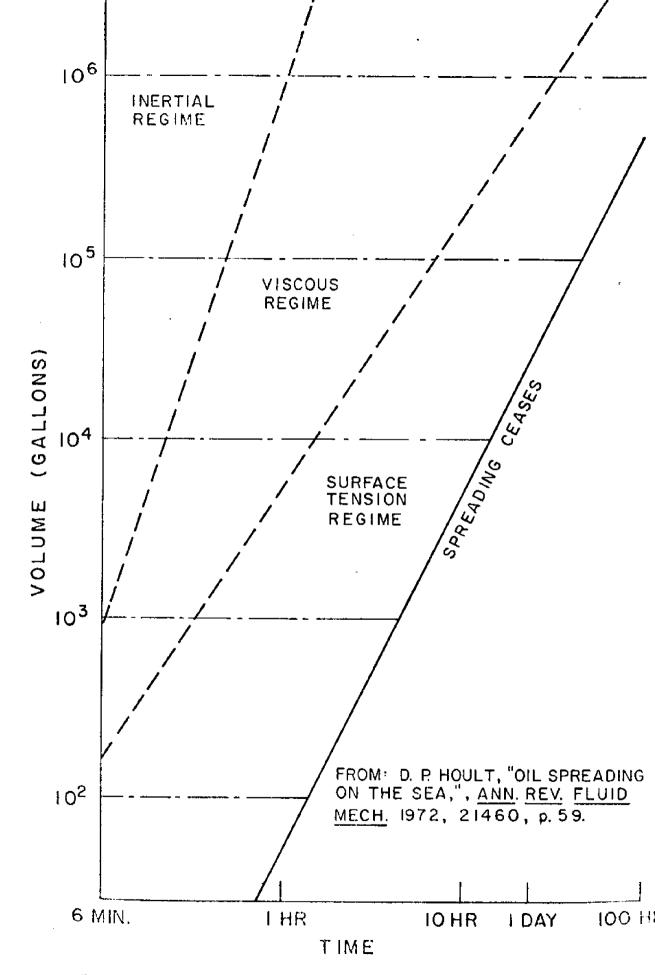
<sup>&</sup>lt;sup>1</sup>This section was prepared primarily by Dr. David Hoult, Department of Mechanical Engineering and Mr. Robert Stewart, Department of Ocean Engineering, M.I.T. The model used here was originally developed for the problem of oil spiils far off-shore. The model has been adapted for near-shore spills and the results should be treated with some caution.

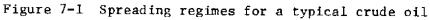
that is, that it is free to spread in all (horizontal) directions. It will be found that the oil spreads at three different rates, depending on when one looks at the spill. Each rate is determined by a unique balance involving various properties of the oil and the water. The first two spreading rates involve balances between the buoyancy induced spreading force, and first the oil's inertia, then later the water's viscous drag. The third spreading rate is due to a balance between the surface tension spreading force and the water's viscous drag. It is convenient therefore, to consider the following three distinguishable phases in the spill's history: an inertial (spreading) regime; a viscous (spreading) regime; and finally a surface tension (spreading) regime.

These regimes will persist for varying lengths of time, depending on how much oil is initially released. Figure 7-1 depicts the varying intervals as a function of the spill volume for a typical crude oil. The shaded line at the right indicates the time at which one can expect all spreading to cease. This is an observed phenomena, and various theories have been developed to explain it. One of the more successful theories was developed by Fay (1971) in which he presumed that the hydrocarbons responsible for the observed surface tension are lost through either evaporation into the air, or dissolution into the water.

Figure 7-2 traces the history of the growth of a spill for several spill volumes, depicting the area covered as a function of time. Again, typical crude oil properties were presumed. Table 7-1 summarizes the various formulas used to generate these figures. Time is measured in hours, volume in gallons, and area in square miles.

In addition to these well-documented spreading phenomena, an oil spill exhibits two other properties that have a qualitative importance to this study. At some time during the spreading process variations in the wind,





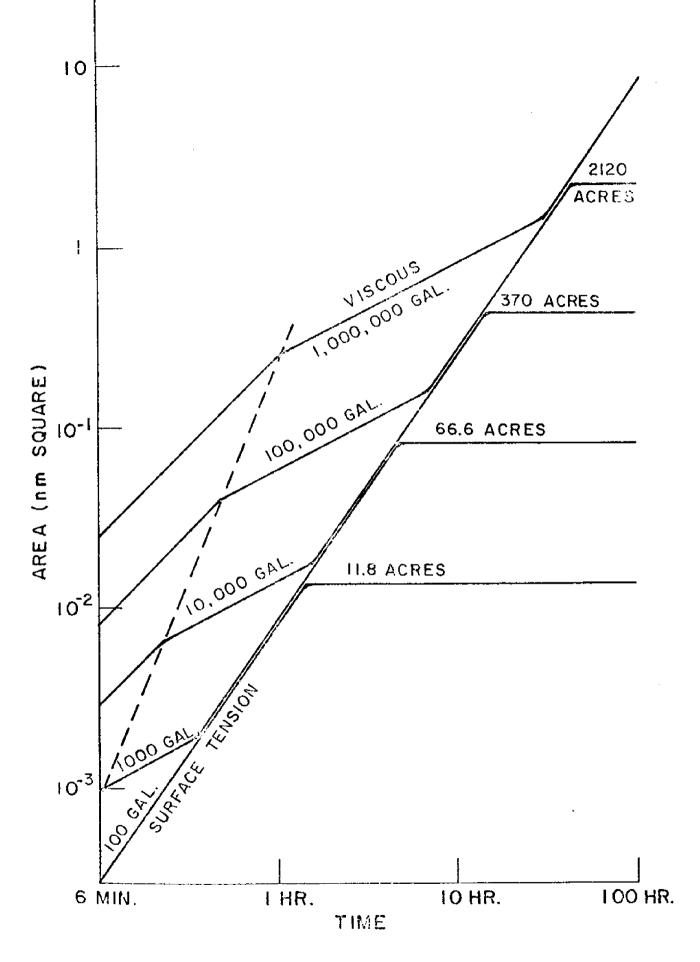


Figure 7-2 Representative spreading histories for five spill volumes, area covered vs. time from spill. Typical crude oil characteristics

	One-dimensional	Axisymmetric
Inertial	$\ell = k_{li} (\Delta gAt^2) 1/3$	$r = k_{2i} (\Delta g V_t 2) 1/4$
Viscous	$l = k_{\rm lv} (\Delta g A^2 t^{3/2} / \nu^{1/2})^{1/4}$	$r = k_2 \sqrt{\Delta g V^2 t^3 / 2/\nu l / 2} l / 6$
Surface tension	$\ell = k_{1t} (\sigma^2 t^3 / \rho^2 v)^{1/4}$	$r = k_{2t}(\sigma^2 t^3 / \rho^2 y) 1/4$

## NOMENCLATURE

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A	Volume of oil per unit length normal to x	Subscripts
g	Acceleration of gravity	1 One-dimensional spread
h	Thickness of oil film	2 Two-dimensional (axisymmetric) spread
k	Proportionality constant	S Maximum area
R	Length of one-dimensional oil slick	i Inertial spread
r	Maximum radius of axisymmetric oil slick	t Surface tension spread
	solubility	v Viscous spread
t	Time since initiation of spread	ow Oil/water
u	Spreading velocity of oil film	aw Air/water
v	Volume of oil in axisymmetric spread	oa Oil/air
x	Dimension in direction of one-dimensional spread	
δ	Thickness of viscous boundary layer in the water underneath the oil film	
σ	Spreading coefficient or interfacial tension (with subscript)	
ν	Kinematic viscosity of water	
π	Absolute viscosity of water	
ρ	Density of water	
Δ	Ratio of density difference between water and oil to density of water	

## Spreading Law Coefficients

	One-dimensional	Axisymmetric
Inertial	kji = 1.5	1.14
Viscous	kjy ≠ 1.5	1.45
Surface tension	k <sub>lt</sub> = 1.33	2.30

waves, and current usually cause the large contiguous spill to break into several large patches surrounded by many smaller patches. The large patches will tend to separate from one another as time goes on. This will increase the width of the path swept by the spill. Additionally, the action of breaking waves on the open ocean, or of surf near shore, may cause a portion of the oil to be mixed into the water column. The importance of this behavior is that the tiny oil droplets suspended in the water can substantially increase the surface area available for diffusion of the oil hydrocarbons into the water. This is certainly of importance in the surf region and may be of importance in the open ocean.

Quantitative prediction of these two phenomnea is beyond current "state-of the art". The model required to estimate the rate at which the large patches will separate from one another is presently the subject of considerable controversy. Various diffusion "laws" have been proposed, but it has been shown that no one law adequately describes a broad spectrum of behavior. In actual spill incidents, this is of little importance because each large patch can be tracked individually. Only for a predictive study is this a serious shortcoming.

The suspension of oil droplets in the water column is related to the turbulence observed in the surface layer. The nature of the dependence of the suspending phenomena on the turbulence is only qualitatively understood. Moreover, the dependence of the turbulence upon the surface waves and wind is unknown. It is known that the energy that the wind imparts to the surface waves is much greater than that which it imparts to the turbulence near the surface. The turbulence is given access to the waves energy when waves break, so in winds great enough to cause whitecaps the surface turbulence increases substantially. The depth to which this strong wave induced turbulence penetrates varies. Phillips (1969) warning that the

available data is fragmentary states that the depth is proportional to the wavelength and cites some published results which indicate that 10 to 30 meters might be a representative range for the depth of penetration of the strong wave generated surface turbulence. Data from the tanker Arrow spill (Forrester, 1971) support this conclusion.

Oil particles will respond to this turbulence as a function of their size, because the rise velocity of a small droplet will be much less than the rise velocity of a large droplet. Utilizing Stokes' formula for the drag on a sphere at low Reynolds numbers it can be shown that the requisite power actually goes as the diameter to the fifth power. Thus, the maintenance of a droplet one tenth the size of another at some specified depth will require one-one hundred thousandth the power. This implies that one can expect small droplets fairly deep, while large droplets should remain near the surface.

Summarizing, formulas have been presented which describe the spread of oil on the surface of the water. The initial rate of spread is dependent upon the volume spilled and is characterized by two distinguishable spreading regimes. A third spreading regime is encountered once the thickness of the spill decreases to a point where the outward pull of surface tension exceeds the buoyancy effects. The spill finally ceases spreading and a predictive equation has been presented to describe this. Additionally, the tendency of the spill to break into patches and the turbulent mixing of oil into the water column have been discussed. In both cases, predictive models do not appear to be available.

7.2.2 Trajectory of A Spill

Wind blowing over the water surface imparts momentum to the water and causes complex motions throughout the water column. In the very top

layer of the water column this motion, when compared to the motion of the rest of the water, will be in the direction of the surface wind, and it will remain so as long as the wind continues to blow (as long as the constant shear layer is maintained). Should the wind die, then Ekman's formula leads one to expect that the water at the surface will be entrained by the underlying water and it will undergo complex cyclic motions at the inertial frequency, which at the latitude of the Gulf of Maine is about 1 cycle per 18 hours. The details of this no-wind motion are complex and of little interest, because the net transport is small. The motion while the wind blows is of importance, however, because substantial transport of the surface layer of water can occur.

In order to specify the magnitude of the velocity of the surface layer, it would seem to be necessary to relate wind speed and wave conditions to the amount of momentum imparted to the water. Achieving this in a detailed way is not yet possible. In fact, the very mechanism by which the momentum is transferred through the water is not fully understood. It is possible, however, to make a reasonably accurate estimate of the net effect of all these phenomena by assuming that the air and the sea behave similarly, and that the ratio of the square root of the densities of air and water is the scaling factor determining the velocity of the water at the surface with respect to the velocity of the wind measured away from the immediate effects of the water (say 10 m high). Based on this, the velocity of the surface layer (SL) is about 3/100 of the velocity of the wind (SW).

This analysis so far has not considered the behavior of the surface water when oil is present. Oil has a calming effect on waves, and it might be expected that some reduction in the transport would occur due to the smoothing of the surface. This is not the case, however, because waves generally are created by the wind and move with the wind. The action of damping waves actually imparts additional momentum to the oil. It is found that the oil actually drifts a bit faster than expected.

It must be remembered that the surface drift due to the wind has been taken with respect to the bulk of the fluid lying under the surface layer. If this fluid is moving under the action of a current, the net motion will be the vectorial sum of the two velocities. Putting all this together, the following formula is obtained, which applies to the center of mass of the oil slick:

 $\vec{u}_{oi1} = \vec{u}_{current} + (.03) \vec{u}_{SW}$ 

This formula has proven to be consistent with laboratory and field observations.

7.3 Data Base

7.3.1 Currents

Currents may be either tidal in origin or, in off-shore regions, complex steady currents due to subtle interplay between the earth's rotation, variations in water density and the meanders of the strong northeasterly Gulf Stream. Peak tidal velocities range from 1 knot to 5 or 6 knots, depending on geography. Steady, non-tidal currents are typically a few tenths of a knot in magnitude.

A distinction between these two types of currents, based on the distance travelled by a slick is helpful. For the purposes of this study regions within harbors and bays are considered to be governed by only the

tidal component. Further off-shore only net transport induced by steady currents is considered.

A detailed search was made of Federal and private data sources for supporting current data. Tidal current charts are available for Boston Harbor, Nantucket Sound, Buzzards Bay, Narragansett Sound, Block Island Sound and Long Island Sound. Tidal currents are also indicated for the Bay of Fundy on Chart H.O. 609, U.S. Naval Oceanographic Office. However, the Maine-New Hampshire Coast is not covered at all. This is obviously a serious flaw because the near-shore problem for Maine is of central importance. The data situation for steady currents is not much better. Graham (1971) summarizes the information that is available (see Section 4).

A review of the literature was made in hopes of finding a more recent validation of his findings. The most recent compilation of the hydrography of the Gulf is given by Colton et al, (1968), and he did not attempt to reduce the temperature-salinity data to sea-water density. Nevertheless, a comparison of data taken one year apart shows considerable variation in the isotherms and isohalines, (see for example, Figure 51, Colton et al, (1968)) which leads one to suspect that a good deal of data, spread out over many years, will be required to establish a reliable statistical base.

Therefore, with the exception of Tidal Current Charts for Boston Harbor, Cape Cod, Buzzards Bay, Narragansett Bay, Long Island Sound and Block Island Sound, little is known of the currents. This is a predicament because the current will be one of the two factors that determine where the oil will go (the wind being the other).

## 7.3.2 Wind Data

The available data on winds is considerably more complete, and the question here is to determine what statistics ought to be used in modeling

the wind. It has been traditional to consider only the mean wind properties in air quality studies. This has led to much emphasis on the wind rose as the principal statistic. The wind rose provides the probability that at any arbitrarily selected time the wind will be blowing from a particular direction at a mean speed (or perhaps in one of several speed ranges). If the phenomena of interest is short-lived, say on the order of minutes or hours, this may be acceptable (for example, the fall-out of soot from a chimney in the region immediately adjacent to the chimney). However, if the phenomena lasts longer then the changes in the wind should become important. In a large number of tests, one would expect the majority of samples to congregate around the mean drift, with some percentage wandering off away from the mean. This behavior, and particularly the deviation from the mean is not simulated by wind rose statistics. At present, there appears to be no generally accepted technique for handling this problem.

In order to investigate the variability of the wind, the wind records from Nantucket Island Airport and Portland (Maine) Airport were obtained for five year periods in the late sixties from the National Climatic Center in Asheville, North Carolina. The wind records were broken out into the traditional eight directions (N, NE, E, SE, S, SW, W, NW) as well as calm, and the persistence of the wind in each direction was determined. This data is summarized in Table 7-2. Note that the average persistence is on the order of 5 to 10 hours. This implies that the wind rose approach to drift predictions is highly inaccurate for phenomena lasting over 5 or 6 hours.

In order to handle this problem, wind is modeled as a first order Markov process. In this model it is assumed that the probability that the wind will change from one state to another is dependent only upon the

Wind Direction	Nantucket (Hours)	Portland (Hours)
N	6.2	3.9
NE	5.2	2.8
E	4.7	3.3
SE	4.6	2.1
S	5.5	4.8
SW	6.1	2.8
W	4.8	4.2
NW	4.3	3.2
CALM	1.7	2.9

## Table 7-2. Average Persistence of Wind Nantucket Island Airport & Portland, Maine Airport

(Seasonally Averaged)

characteristic of the wind at the moment of transition. In this terminology the word state refers to some unique direction and (perhaps) speed range. Thus the Markov model allows one to determine some measure of the probability that the wind will change from North at 10 knots (for example) to Northwest at 17 knots. Various investigators have had considerable success in using these techniques when applied to other physical phenomena, and with the proper selection of "states" a reasonable model for wind is obtained.

The states selected consisted of a simple system comprised of N,NE,E,SE,S,SW,W,NW, and calm. The probabilities are contained in a nine by nine matrix, a sample of which is shown in Table 7-3. The matrix is used as follows: Enter the matrix in the row corresponding to the wind direction at present. The numbers in the column elements of that row give the probability that the wind will be from the column's direction after 3 hours. The speed presumed for the wind is the average for that direction. This simulation of the wind has some inherent inaccuracies, especially the underestimation of the persistance of the wind over more than one transition. However, this leads to an overestimate of the probability of changing directions which should lead to the conservative result of an overestimate of the dispersion (conservative in the sense that this generally increases the chance of an arbitrary point being hit by a spill).

The winds along the Maine Coast are presumed to be properly represented by the Portland, Maine, Airport wind data. Because the extreme northern edge of the study area is about 150 nautical miles from Portland, some variation in the behavior of the wind is expected. However, the assumption appears to be valid relative to other data gaps and inaccuracies. 7.4 Simulation Technique

In view of the foregoing discussion of the variability of the wind,

				_	<u> </u>	-	<b></b>		
	CALM	N	NE	Е	SE	S	SW	W	NW
CALM	0.384	0.149	0.034	0.040	0.037	0.065	0.065	0.142	0.084
N	0.059	0.464	0.138	0.053	0.025	0.006	0.019	0.059	0.176
NE	0.031	0.340	0.340	0.170	0.062	0,005	0.010	0.031	0.010
E	0.066	0.056	0.112	0.391	0.157	0.168	0.010	0.020	0.020
SE	0.062	0.049	0.025	0.167	0.315	0.265	0.062	0.025	0.031
S	0.084	0.021	0.007	0.009	0.067	0.550	0.190	0.058	0.014
SW	0.099	0.029	0.019	0.003	0.019	0.178	0.363	0.261	0.029
W	0.104	0.060	0.012	0.012	0.012	0.044	0.129	0.504	0.124
NW	0.073	0.236	0.035	0,035	0.010	0.051	0.026	0.169	0.364

Di	Wind irection	Percent Observed	Mean Wind Speed	RMS	S	E
	CALM	11.092	0.000	0.000	0.000	0.000
	N	16.312	6.661	3.322	+0.994	0.909
	NE	6.662	6.588	2.949	+0.920	0.842
	E	6.765	6.670	2.739	+0.979	1.485
	SE	5.563	7.093	3.812	+1.025	0.459
	S	14.835	7.725	3.301	+0.535	0.130
	SW	10.783	6.369	3.103	+0.998	0.983
	W	17.239	7.092	3.786	+1.132	1.400
	NW	10.749	6.629	3.782	+0.906	0.148

Portland Airport: Autumn 3 Hourly Transition Matrix

and its importance in determing spill trajectories, a simulation technique is sought which allows one to accommodate probabilistic behavior. The simplest and most straightforward appears to be the use of a Monte Carlo model. The model was based on the simple trajectory equation given earlier, with the current being treated as a deterministic quantity which can be assigned direction and speed values as a function of location. The wind is modeled as the nine-state Markov process just discussed. The wind changes with the seasons, but the current remains fixed.

The broad outline of the computer program used to execute this technique is fairly simple. Basically, a sample spill is released at a specified point. The initial wind direction is determined from steady state statistics. The spills velocity is then computed and its progress is traced. Every simulated three hours the Markov matrix is entered and a new wind value is randomly selected according to the probabilities given by the matrix. The program also updates the current velocity and even the season as required as the spill moves from one location to the next, or from one season to the next. As the spill progresses on its trajectory the computer keeps testing to see if the spill has either impacted land or washed out of the region of interest. Each sample spill is allowed to go for 150 simulated days before it is cast off and a new sample spill released. The process is repeated 200 times, that is, 200 sample realizations are made, for each season and launch point. The accuracy that can be expected from such a process (if there were no inaccuracies in the input data) is on the order of plus or minus a few percent (1% to 6% depending on certain features of the problem) to a high degree of confidence. This could be reduced by running more than 200 sample realizations (say 1000), but it was felt that other errors particularly in the current specifications

were so much greater that nothing significant was to be gained from such a decision.

In coastal areas the extent of spreading is significant, and the treatment of the spill as a contiguous slick is fairly well justified. Therefore, the radius of the slick is computed and the points of impact of the slick are determined using this radius.

7.5 Catastrophic Spills

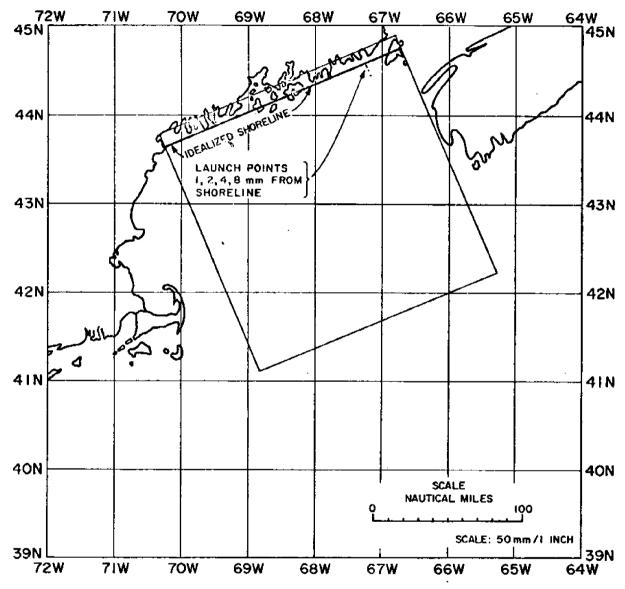
As mentioned previously, in harbors or bays having high peak tidal currents, the major portion of the transport process will be by tidal current alone. This presents serious problems from an analytical standpoint because the variations in tidal current velocity from one point to the next causes distortion and even separation of the slick surface. For example, consider a slick several miles across being washed directly onto an island within a bay. The current flows around the island dividing the slick into two parts (as well as coating the island's beaches). As this process is repeated over and over the slick is broken into more and more individual patches. As the number of patches increases the number of beachings increase and soon the whole problem blows up, because the model cannot account for the oil stranded in beaching or refloated in a rising tide. The prevailing winds has some influence on the trajectory, but because only three percent of the wind velocity applies to the slick motion, it takes very strong winds to even approach the effect of a one or two knot tidal current.

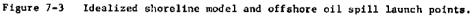
Superceding the above arguments is the fact that the tidal currents for Machias Bay, Maine are quantitatively unknown (with the exception of a few velocities reported for isolated passes or points). Thus, analysis within a Maine coast harbor is completely infeasible.

Qualitatively, an extrapolation from the Tamano spill in Casco Bay, Maine can be made: any spill whose final area is within one or two orders of magnitude (within a factor of 10 to 100) of the area of the bay in which the spill occured poses a very real threat to all the beaches in the bay. Although this is a rather sweeping generalization based on qualitative speculations it is highly reasonable in light of the large tidal currents and excursions which occur in the Machias Bay region.

A problem that does yield to analysis is the extent of the hazard posed by the proposed terminal location. That is, is a terminal in Machias Bay a problem that only affects the people of Northern Maine, or can the waters of Portland, Maine also be affected by a Machias spill? The problem fits into the methodology previously discussed because boundaries for the problem can be constructed in such a way that the areas of strong tidal current are excluded from the problem. It is simply assumed that once a spill gets into waters with strong tidal currents that the spill is washed about sufficiently to coat the beaches in that immediate area. Figure 7-3 shows one possible use of this assumption. It can be seen that there are four launch points off the idealized shore. They lie 1, 2, 4, and 8 miles from this shore. The currents immediately off the Maine coast are uncertain. but it is in line with most available data (Graham, 1971) to presume that current velocities are between zero and a uniform southwesterly current at about .3 knots. Consequently, a variety of possible current patterns within this range are used to determine the variation in transport behavior caused by the current.

There is some question concerning the volume dependence of the phenomena. The spreading equations allow one to determine the size of the slick, but the dimensions are not the only parameters of interest. If the slick goes ashore, clearly more oil will be refloated on the next tidal cycle if

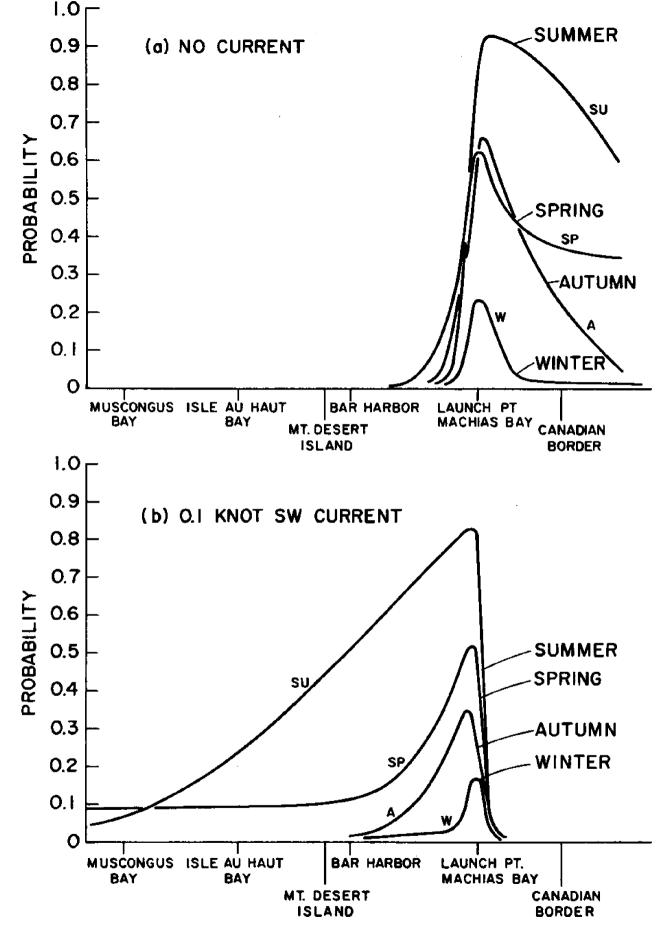




the amount deposited initially is increased. Thus a very large slick will have many more secondary (and tertiary) relaunchings of the spill than will a small slick. In order to cope with this problem, two extremes of behavior are postulated. On one hand, the transport distance will be the least of all, the oil that crosses into the tidal region is absorbed on the beaches of that region. This presumption neglects secondary relaunchings of the spill and further presumes that all the oil will hit a beach or other absorbing obstacle, rather than wash in with the tide and then wash back out. This behavior might be considered "best" case, because it will tend to cause the spill to be limited to a much more localized region.

A "worst" case behavior can be constructed by presuming that none of the spill is absorbed upon crossing into the tidal region, but rather, it is stored in that position until the winds and current are favorable for another trip up or down the coast (or out to sea). This worst case behavior can be considered to mimic at least the transport of the remnants of a spill long after it has ceased to be a large contiguous mass. An actual spill would tend to fall in between the two extremes, possible lying closer to the latter than the former.

This analysis was carried out for a one million gallon spill from each of the four launch points, for each season. Figures 7-4 through 7-6 summarize the results for the launch point one mile offshore. Figure 7-4 shows the seasonal probabilities that a 1.8 nautical mile length of shore will be touched at least once given a spill occured one mile off the idealized coastline at Machias Bay, presuming that the coast is non-absorbing. This represents the "worst" cast result, or alternatively, the extent to which remnants might travel down the coast. No current and a very slight SW current were found to cause the widest variation in behavior. The 0.3 knot SW



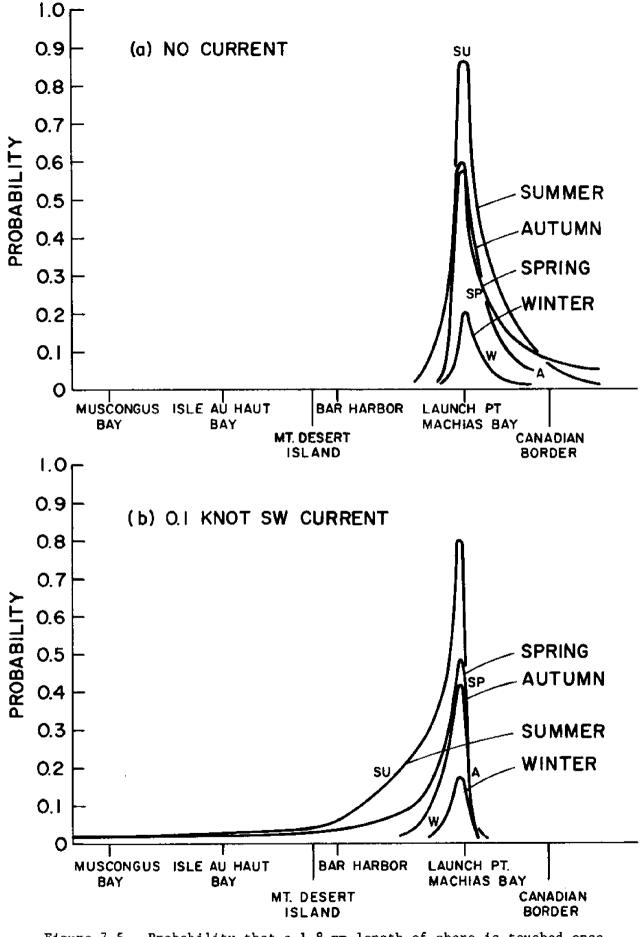
Fugure 7-4 Probability that a 1.8 nautical mile (nm) length of shore is touched once during the life of a spill. (non-absorbing, idealized shoreline, one million gallon spill, launch point one mile off idealized shore)

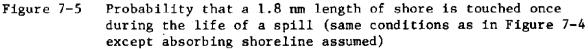
current was less influential in generating undesirable results because its offshore component was strong enough to cause the spills to be washed out to sea, except for a very particular wind pattern.

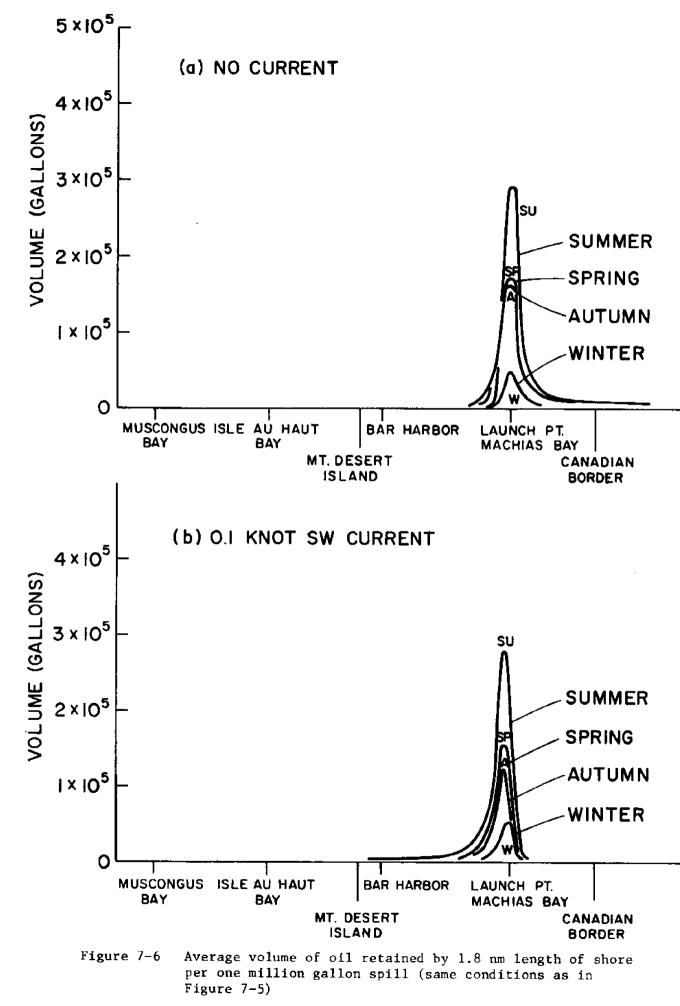
It is speculative, of course, to presume that the current is slightly offshore rather than parallel to it, but one of the main driving forces would seem to come from the surface run off of fresh water from the various rivers emptying into the Gulf of Maine, and this should cause a net outward motion. This observation is reinforced by sea bed drifter experiments in which it was shown that the bottom waters of the Gulf of Maine lying near the Maine coast are drawn up into major estuaries to replace water that was apparently entrained by the overlying rresh water and then carried out to sea. The along-shore component of the sea bed drifters' trajectory was usually in a northeast to southwest direction, substantiating our basic presumption (see Graham 1970, Figure 3).

Figure 7-5 shows the results from the "best" case (absorbing) analysis. Again, the parameters displayed are the chance that a 1.8 mile length of idealized shoreline will be touched at least once versus location along the coast. Figure 7-6 displays the average volume of oil that would be absorbed by the absorbing shoreline along a 1.8 mile length, as a function of its position.

The main conclusions to be drawn from these graphs are that once again the current behavior is crucial in specifying the basic drift of the spill (once again the currents make the choice between U.S. and Canadian beaches). Once again, the phenomena is highly seasonal. And finally, while the probability of finding remnants of an oil spill is .2 or more all the way from Penobscot Bay to the Canadian Border during summer, the average volume deposited on an absorbing shoreline in a spill incident is highly localized about the launch point.

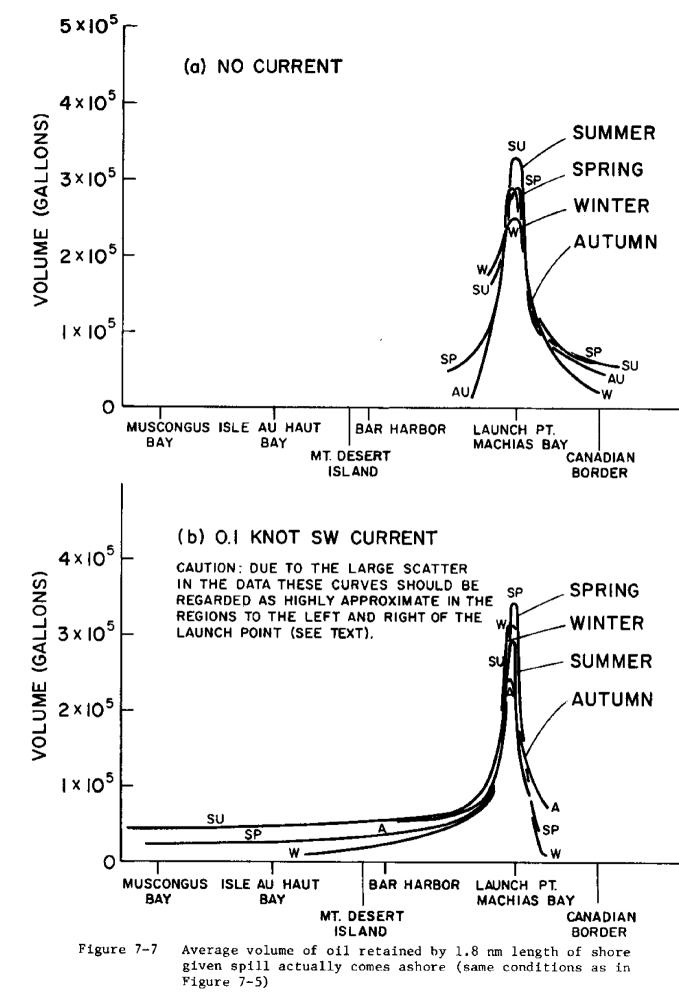






The average volume figure is somewhat misleading as it includes both spills that come ashore and those that do not. This is the average amount of oil one would expect to collect every 1 million gallon spill incident after observing many incidents along a 1.8 mile length of shore. Another figure of interest, therefore, is the amount of oil deposited on a 1.8 mile length of shore counting only those spills that go ashore. This data is presented in Figure 7-7. The curves tailing to the left of the launch point should be regarded as being highly uncertain due to both the small number of realizations available for the mean value computation, and due to certain artifacts caused by the determinisitic transition step size presumed in the model of the wind transport. The data is sufficiently accurate, however, to make the generalization that near the launch point, a 1.8 mile length of shoreline can expect to receive approximately 3 x 10<sup>5</sup> gallons from a 1 million gallon spill. More than seven or eight miles away from the launch point, this value drops to less than  $1 \times 10^5$  gallons per 1.8 miles of shoreline, and is probably in the range of  $3 \times 10^4$  gallons to  $5 \times 10^4$  gallons. Also it is presumed that all the oil that crosses the idealized shoreline is retained. In practice, this assumption is probably much too optimistic. It seems certain that if the oil is not removed through some cleanup activity, then a substantial fraction will be left for further transport up or down the coast. This implies that the estimates are merely lower bounds. No technique for estimating an upper bound (short of the total volume spilled) seems feasible.

Another topic of interest is what are the trade-offs involved with an offshore, single point moor versus an onshore intertidal terminal concept. Utilizing the four launch points the percentage of spills that washed ashore is computed for each season. This computation considered only the motion of



the center of mass of the spill. The results of this analysis are shown in Figure 7-8. Note that if there is a .3 knot southwesterly current, locating the mooring point farther out greatly diminishes the probability that the spill will be blown ashore. If there is no current, then the same statement generally holds, except for summer, when just about everything spilled will be blown ashore. These results are independent of volume, as the trajectory of the center of mass of the spill was used to determine impact. Not shown in this figure are the spill trajectories if it does not impact on the idealized coastline. For the no current case, the spills will almost invariably end up in the Bay of Fundy. For the .3 knot southwesterly current, one can expect a sizeable fraction to impact on the New Hampshire coast and the Massachusetts coast, including the north side of Cape Cod (Figure 7-9).

In addition to the one million gallon spill discussed in previous paragraphs, a ten million gallon spill was investigated for the .1 knot SW current and the absorbing shoreline presumption. The anticipated results were that (a) the probability of a length of shore being touched at least once would increase, particularly in the tail of the distribution, and that (b) the amount of oil absorbed per length of shoreline would also increase. These proved to be generally the case. Figure 7-10 shows the probability that the shore will be touched at least once in the life of a ten million gallon spill, presuming the shore behaves like an absorbing boundary. Note that the probabilities near the peak are almost identical to those of Figure 7-5, but that in the portion of the tail immediately to the left of the peak, the probabilities are nearly twice as large, being on the order of 10% during summer at approximately M. Desert Island, 3 or 4% for the one million gallon spill at the same point. Far to the left, the probabilities tend to lie together in the 1 to 2% range.

The average amount of oil deposited on a 1.8 mile length of shore per

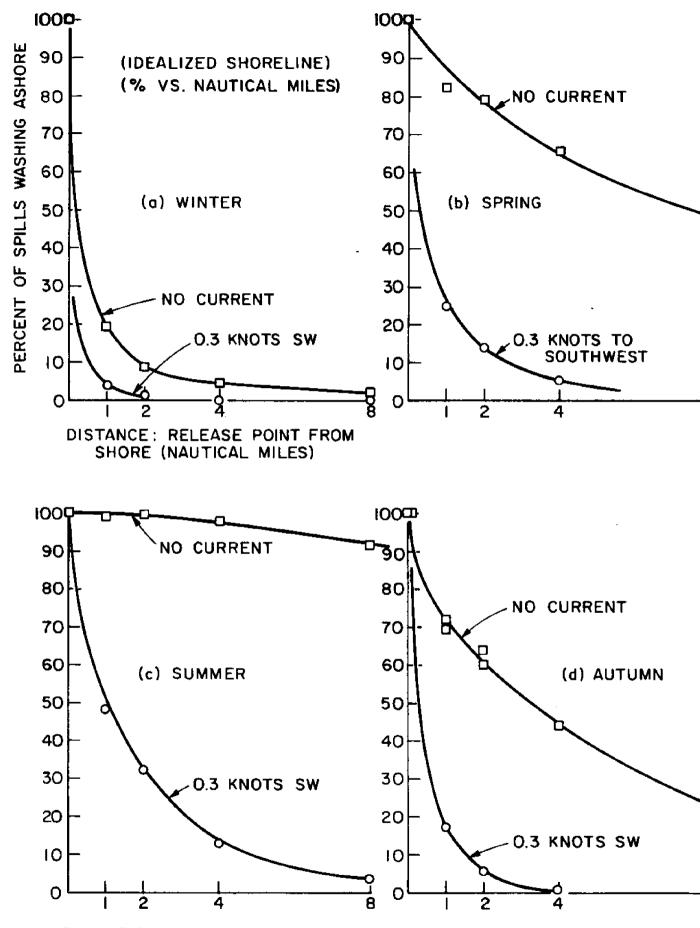
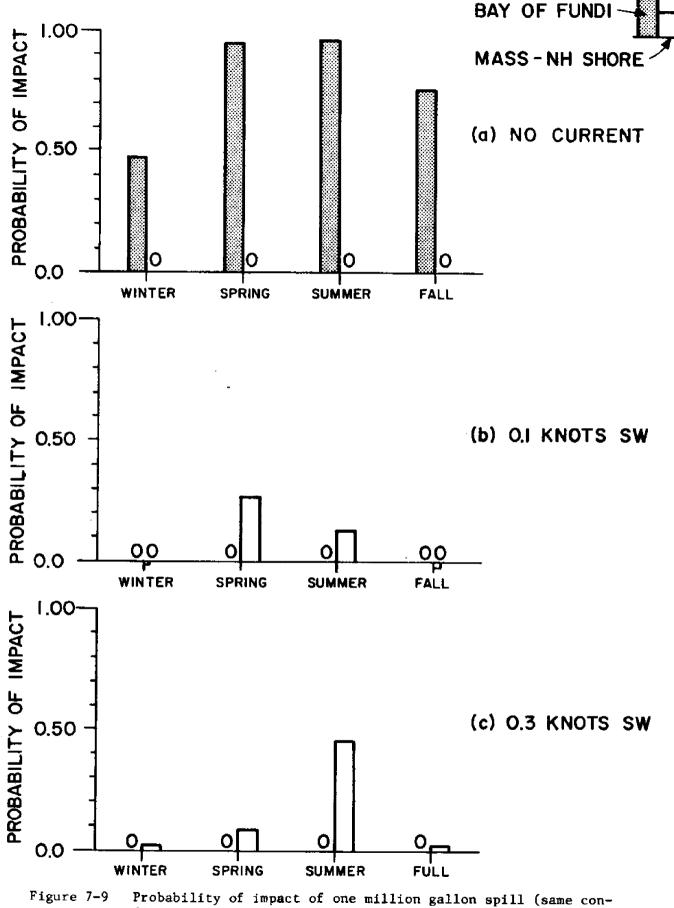
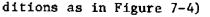


Figure 7-8 Seasonal probability that a spill will be washed ashore for various launch points (absorbing shoreline, one million gallon spill)





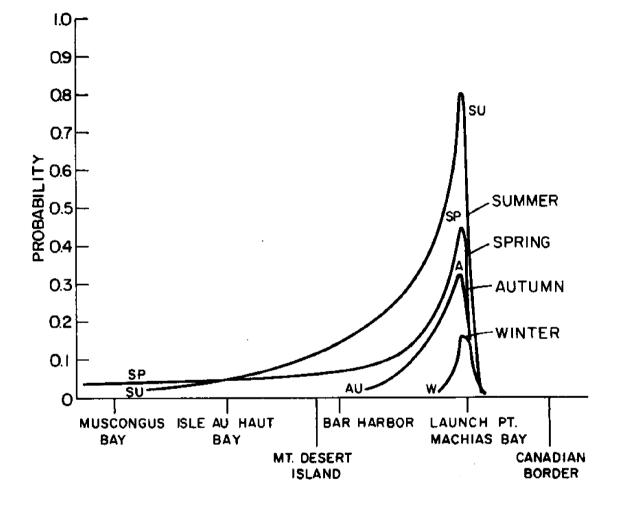


Figure 7-10 Probability that a 1.8 nm length of shore is touched once during the life of a spill (same conditions as in Figure 7-5 except a ten million gallon spill)

spill incident was determined and it was found that except for a factor of ten, the curves of Figure 7-6 depicted the behavior fairly well. The significant difference lay in the amount of oil deposited in the region far to the left of the launch point. In this region, the amount of oil deposited was small in proportion to the amount launched, so the graphic representation utilized in Figure 7-6 would fail to show the difference between zero and this amount. However, the amount was still substantial from a pollution standpoint. Table 7-4 summarizes this effect by noting the distance south to the last point impacted by a portion of the original spill and the amount deposited for the one million and ten million gallon spills, for each season. Because these results derive from the tail of this distribution, the uncertainty in these numerical values is large. However, the order of magnitude is probably accurately determined. Note that the values still tend to be different by approximately an order of magnitude, indicating that the spills do not rub down the shoreline, slowly losing material, but rather, they probably impact it once or twice prior to their final collision, bouncing well offshore in between impacts, and then drive themselves completely into the tidal region.

It must be remembered that the assumption of the absorbing shoreline is our "best" case result, giving a lower bound on the region affected. In an actual spill incident, one might say that the behavior of a large patch of the original slick is given by this estimate. However, remnants due to secondary launchings or excursions into tidal regions that did not result in headings would increase the volume flowing south and the probability that a length of shore would be polluted.

Results for a 100,000 gallon spill are not shown. However, they do not differ qualitatively from the results of the one million and ten million gallon spills. 7.6 Chronic Spills

The trajectory of chronic spills are not analyzed in detail in this

Winter	57 (Isle Au Haut Bay)	9 x 10 <sup>3</sup>	57 (Isle Au Haut Bay)	1.6 x 10 <sup>5</sup>
Spring	130 . (Portland)	2.8 x 10 <sup>4</sup>	130 (Portland)	2 x 10 <sup>5</sup>
Summer	97 (Muscongus Bay)	6.4 x 10 <sup>3</sup>	102 (Muscongus Bay)	5 x 10 <sup>4</sup>
Autumn	40 (Bar Harbor)	1 x 10 <sup>3</sup>	49 (Mt. Desert Island)	3.6 × 10 <sup>4</sup>
				C

Distance to Last Impact Amount Deposited Point, Measured South Given Spill Hit

Amount Deposited Given Spill Hit Shore\* (gallons)

Impact

Distance to Last Impact Point, Measured South from Machias Bay (NM)

Season

One Million Gallon Spill

from Machias Bay (NM)

Ten Million Gallon Spill

Given Spill Hit Shore\* (gallons)

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*Note:

Table 7-4

report. James (1972) has reported analysis of chronic spills which is sufficient for the purposes of this study. These results are given in Table 7-5. Initial plume width refers to the width necessary for the slick to appear as bright bands of color (approximately .0003 mm). Final plume width refers to the width at which the average oil concentration is less than ten gallons per square mile, at which time the oil is no longer visible to the eye. The time required to proceed from the initial plume width to the final plume width is given as a function of different dispersion coefficients.

Table 7-5 Area of visible influence of chronic spills (from James, 1972)

Barrels Per Day	Initial Plume Width ft. m		Final Plume Width ft. m		Time Required in hrs. D_=50 D_=100 D_=200 y y y			Length km	Area (km) <sup>2</sup>
1.2	200	60	2,000	600	1	0.5	0.2	0.5	0.2
2.3	400	120	4,000	1,200	4	2	1	2.2	1.4
4.2	600	180	6,000	1,800	9	4	2	5.	5.

### 8. ASSESSMENT OF ENVIRONMENTAL VULNERABILITY

### 8.1 Introduction

The previous material provides a basis for making the actual assessment of the vulnerability of the Machias Bay region to oil supertankers. As illustrated in Figure 3-6, the primary problem is to determine the probable biological effects of hypothetical oil spill events in Machias Bay associated with the terminal operations. Also, the impacts of non-oil spill events must be identified. Ideally, this would be achieved using mathematical models which represent the important characteristics of the Machias region relative to the events of interest. Numerous hypotheses, events and scenarios can be explored using a model, providing an extensive simulated data base upon which to base evaluation of assumptions and final assessment of vulnerability. Unfortunately, time constraints have prevented the synthesis of the many aspects of the particular problems under study here into a mathematical model. Although the complexity of the problem and high levels of uncertainty would indicate the need for caution in the use of a model, the exercise of assembling a model can be valuable in identifying levels and sources of uncertainty.

As a result, the prediction of biological effects which follows is qualitative and incomplete. However, a sufficient indication of the expected impacts is obtained to make a preliminary assessment of environmental vulnerability.

Section 8.2 describes the expected effects of catastrophic and chronic oil spills (see Section 2) on the intertidal, sub-tidal and pelagic areas of the Machias Bay region. The impacts of non-oil spill events are treated in Section 8.3.

### 8.2 Oil Spill Events

### 8.2.1 Catastrophic Spills

Both 500 ton (150,000 gallons) and 30,000 ton (10,000,000 gallons) spills are considered in this section. The possible trajectories of these spills is discussed in Section 7.5. The extent and location of shoreline impinged by a particular spill is dependent upon the location of release, time of year and assumption regarding currents (both tidal and uniform). In order to gain an understanding of the range of possible effects of a single spill, two extremes are hypothesized: 1) a 30,000 ton spill in the mouth of Machias Bay between Libby Island and Cross Island; and 2) a 500 ton spill four nautical miles outside the mouth of Machias Bay (see the idealized shoreline shown in Figure 7-3).

The biological effects of these, or any other spills, depends heavily upon the amount of water soluble aromatic derivatives in the slick as is discussed in Section 6. Due to weathering processes (Section 5.4) the soluble fractions (boiling point< $220^{\circ}C-250^{\circ}C$ ) which are the most toxic materials are removed rapidly and within 48 to 96 hours are probably reduced to a few percent or less of their original amount. In addition, therefore, the original composition of the spilled material can also be expected to influence the biological effects. However, as shown in Table 5-4 the differences between crudes A and B (Table 2-1) are not sufficient to distinguish them in this context.

### 8.2.1.1 A 30,000 Ton Spill

Probably the worst spill case conceivable biologically is the release of a 30,000 ton slick in the mouth of Machias Bay at low slack tide. It is safe to expect that virtually the entire shoreline of Machias Bay would be coated by crude oil within 24-48 hours. Such an event would be a biological disaster. Intertidal zones would be heavily coated with fresh oil, which

could be expected to contain sufficient soluble aromatic components to expose all organisms to concentrations well in excess of 100 ppm. As a result, most species of intertidal organisms would be threatened with lethally toxic concentrations (see Table 6-10). The most serious damage in the intertidal zone would possibly occur in mud flats and other unconsolidated sediments. The heavy oil coating could lead to permanent changes in substratas, preventing recovery of damaged areas, especially the recovery of clams (<u>Mya arimaria</u> bloodworms (Glycera dibranchiate) and sand worms (Nereis vinins).

Also, the potential damage to the few salt marshes is extensive. Many organisms not killed outright would be expected to ingest significant concentrations of hydrocarbons, causing tainting of edible species, especially shellfish. The extent of such a disaster could be compounded if it occurred during the summer and fall when lobsters move into inshore areas. Not only would the individual organisms be threatened, but more importantly, spawning behavior could be disrupted and larval stages killed.

In addition to damage to the Machias Bay coastline itself, significant amounts of spilled oil would be expected to come ashore outside Machias Bay. Figures 7-4 through 7-6 indicate the extent of idealized shoreline hit by a 1,000,000 gallon spill released one mile offshore. This would be equivalent to 10% of the 30,000 ton spill drifting out to a point one mile offshore. (This is a reasonable assumption). Figure 7-4 indicates a significant probability that oil could reach at least as far south as Penobscot Bay or as far north as the Canadian border and well up into the Bay of Fundy. In addition, shoreline outside Machias Bay could expect to be covered by as much as 20,000 gallons of oil per mile (Figure 7-7). The biological damage of oilings outside Machias Bay would be expected to be less extensive. The oil would be more extensively weathered and therefore less toxic. Coating, habitat

changes and tainting could be expected in localized areas.

As extensive as the damage from such a spill might be, long-term damage to higher levels of biological organization may not be as far reaching. Populations of benthic invertebrates in unconsolidated sediments would be the most seriously threatened, especially burrowing crustaceans and worms. The recovery after a single event would probably be complete in 2-3 years for most species. Generally, low temperature in the Machias area would cause recovery to be slower than in more temperate regions. Major long-term shifts in the community and ecosystems are not likely. Nearly all marine populations have evolved mechanisms for reproduction which provide a high probability of species survival (and therefore community and ecosystem survival) in the face of major natural environmental disasters such as hurricanes which may cause disastrous changes in, say, seawater salinity. In particular, most marine plants and animals are "r strategists" (Section 3.2) producing many more offspring than the environment can support, but ensuring survival of the species by only a few adults.

The scenario described above assumes that the 30,000 ton spill occurrs at low slack tide in the mouth of Machias Bay. If the spill occurred further offshore, damage would probably be somewhat reduced, but still a major disaster. Furthermore, considerably more oil would be expected to find its way north or south of Machias. In effect, the localized effects would be less extreme, but the area affected could be increased markedly. 8.2.1.2 A 500 Ton Spill

A 500 ton spill released in the mouth of Machias Bay at slack tide would also be expected to pose a serious threat to the Machias Bay coastline, not unlike that described above. However, it is not likely that oiling

outside Machias Bay would be as extensive as that envisioned for a 30,000 ton spill.

In contrast to the scenario of a spill released at the Machias Bay entrance it is instructive to consider a spill released several miles offshore. It is clear from Figure 7-8 that the probability of the slick coming on shore is reduced significantly for the hypothesis of a .3 knot southwest current along the coast. For the hypothesis of no current, releasing a spill further off shore may reduce the probability somewhat, but not drastically. In fact, as was indicated in Section 7-5, in the summer, almost any oil spilled may be expected to come ashore.

The primary considerations causing differences in biological effects by an off shore spill is the increased weathering time and greater dispersion of oil that will take place. Damage could be expected to be from coating and to a lesser extent, lethal toxicity as described in Section 8.2.1.1. No doubt the rocky islands along the coast would take the brunt of the damage, but some oil could be expected to find its way into the bays and estuaries, and therefore mud flats and salt marshes. In general, non-lethal damage such as tainting and changes in substrate texture would be likely to be more extensive than direct killing of many organisms. Recovery in areas covered by oil could be shorter than in the case of a 30, 000 ton spill due to less intensiveness of the damage.

The primary problem associated with 500 ton spills is that one can be expected to occur on the average of once a year (Section 2.2). Therefore, on the average, several miles of shoreline would be hit by an oil slick. This can be expected to lead to serious long-term biological damage in areas near the entrance to Machias Bay, which have a high probability of being hit by the oil (see Figures 7-4 and 7-5). Repeated coverings would prevent recovery and lead to permanent shifts in the species composition to highly resistant organisms, such as some kelps and gastropods.

### 8.2.2 Chronic Spills

Chronic spills do not pose a major biological threat. Table 7-4 shows the area for spills of 1.2, 2.3 and 4.2 Bbls per day. The initial plume width is based on rapid spreading to a concentration of 200 gallons per square mile (James, 1972). This is equivalent to a concentration of 1 ppm of total hydrocarbons if the oil is assumed mixed in the top two meters of the water column. Within 1-10 hours the concentration is reduced to 10 gallons per square mile or 50 ppb total hydrocarbons. The only expected consequences of these discharges would be tainting of organisms in the immediate vicinity of the terminal. Because of relatively high tidal currents in the area near the terminal, flushing would be expected to be sufficient to prevent accumulation of hydrocarbons in the water. Compared with a 500 ton (150,000 gallons) spill once a year and a 30,000 ton (10,000,000 gallons) spill once in twenty years, the chronic spillage would contribute 555 barrels (28,000 gallons) of oil per year to the Machias Bay region, or less than 5%.

### 8.3 Non-spill Events

The impacts of non-spill events would be minimal for the Machias Bay region. Dredging typically poses the most serious problems, but no dredging is required Rounsefell (1972) has reviewed the potential ecological effects of marine construction and concludes that little damage can be expected from construction and installation of structures. The most extensive construction and alternations necessary for a terminal in Machias Bay are the large breakwaters necessary to protect the berthing facility. Because the rocky habitat is common to that region there would be little effect expected. The effect of these structures on currents and sediment movement in the entrance to Machias Bay is unknown due to a lack of data.

Scouring from ship traffic is not expected to be a problem because of the naturally high currents and deep water.

8.4 Summary

Based on the foregoing discussion it is consluded that the Machias Bay region environment is highly vulnerable to a supertanker terminal. The problems are posed almost entirely by the potential biological damage from oil spills, as opposed to non-oil spill events.

Given that a catastrophic spill occurs, some biological damage is inevitable. If the spill is a 30,000 ton spill, the effects are very likely (more than a 50% probability to be extensive biological damage which, although not irreversible, would take several years for recovery. Smaller more frequent apills would have a nearly equal probability of leading to localized permanent shifts in biological community structures.

The vulnerability of Machias Bay might be less if the probability of these events was small. However, the probability of these catastrophic events is likely to be higher in the Machias region than any other point along the eastern coast of the United States. The coast is rocky, exposed and subject to severe storms and long periods of fog and extremely poor weather (see Section 4). The estimate of one 500 ton spill per year reflects the extreme conditions found along the northern Maine coast.

### 9. CONCLUSIONS AND RECOMMENDATIONS

# 1. The environmental vulnerability of the Machias Bay region to oil super-

### tankers is very high.

An oil spill of 30,000 tons can be expected to occur as frequently as once in twenty-years. If such a spill is released at the entrance to Machias Bay, extensive biological damage is virtually certain of occurring in Machias Bay. A spill further offshore would probably produce a less intensive damage biologically, but would be distributed over a greater area. A 500 ton oil spill occurring on the average of once a year can also be expected. Permanent localized damage is highly probable. Several miles (say 10-20 miles) of shoreline should be covered by each spill and the coastline in the immediate area of Machias Bay has a 10-50% probability of being hit by any large spill released offshore.

# 2. Chronic spillage does not contribute significantly to the environmental

### vulnerability of the Machias Bay region.

Oil spills occurring from day-to-day transshipment operations at the tanker berths are relatively insignificant environmentally. Concentrations of hydrocarbons would be reduced to 50 ppb within a few hours of release of the oil. Flushing would be rapid due to high tidal currents, preventing accumulation of hydrocarbons in the water columns. Some localized tainting of organisms around Stone Island could result from these discharges.

# 3. <u>Non-oil spill activities are also little threat environmentally.</u>

Terminal construction and tanker operation are activities potentially leading to biological changes. However, no dredging is required for construction and proposed structures do not involve major shifts in habitats. Currents in the area are typically of the order of 2-4 knots and tanker traffic is not expected to contribute to the scouring that occurs naturally. The effect of breakwaters on circulation and flushing is unknown because of lack of data on currents.

4. Oil spilled in Machias Bay can be expected to reach as far south as the

New Hampshire coast and as far north as the northern end of the Bay of

### Fundy.

The combination of wind and coastal currents produces an oil drift pattern which transports most of the spilled oil parallel and onto the shore, rather than out to sea. Large spills would lead to many smaller spills as the oil slick dispersed, some of which have a high probability of being transported large distances up or down the coast.

# 5. The water soluble aromatic fractions of oil are the major cause of lethal

and sub-lethal effects of oil on marine organisms.

Most marine organisms are affected, due to cellular level disruption, by aromatic compounds in concentrations in water of less than 50 ppm. The effect may range from immediate death to disruption of behavioral characteristics by concentrations as low as 10-100 ppb. Water soluble paraffin fractions may also be toxic, but at higher concentrations in water than would be obtained from an oil spill. All types of hydrocarbons may be incorporated into tissue by many organisms, which may lead to tainting and/or accumulation of polycyclic aromatic hydrocarbons in food chains.

6. Future research on the effects of oil on marine organisms should focus on

sub-lethal effects, especially disruption of behavioral characteristics

### and accumulation in food chains.

Sub-lethal effects of oil on individual organisms may be as damaging to species populations in the long-term as direct lethal toxicity. Population survival depends upon maintenance of successful reproduction behavior. Low concentrations (10-100 ppb) of soluble aromatics may inhibit mating without killing the organisms outright, ultimately causing the population numbers to decrease. However, there has been little research reported on this important problem upon which definitive conclusions can be made.

7. Research efforts should also focus on development of mathematical models

to investigate the success of dispersal and reproduction strategies for

recovery of populations and communities subject to major environmental

### perturbations such as oil spills.

An important aspect of the ultimate effect of changes in environmental quality is the rate of recovery and ability to maintain an adequate population level following a major impact. One valuable approach to developing insights to this problem is the application of mathematical models. Numerous hypotheses and scenarios may be investigated which can indicate the potential success various organisms may have, as well as identify laboratory and field data needs.

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