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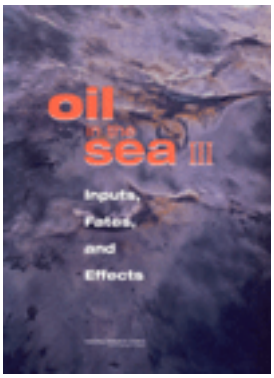

Oil in the Sea III: Inputs, Fates, and Effects

Committee on Oil in the Sea: Inputs, Fates, and Effects, National Research Council

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oil in the sea III

Inputs, Fates, and Effects

Committee on Oil in the Sea: Inputs, Fates, and Effects
Ocean Studies Board and Marine Board
Divisions of Earth and Life Studies and Transportation Research Board
NATIONAL RESEARCH COUNCIL
OF THE NATIONAL ACADEMIES

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This report and the committee were supported by grants from the Minerals Management Service, the American Petroleum Institute, Environmental Protection Agency, U.S. Geological Survey, the Department of Energy, U.S. Coast Guard, the National Ocean Industries Association, the U.S. Navy, and the National Oceanic and Atmospheric Administration. The views expressed herein are those of the authors and do not necessarily reflect the views of the sponsors.

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This report has been reviewed in draft form by individuals chosen for their diverse perspectives and technical expertise, in accordance with procedures approved by the NRC's Report Review Committee. The purpose of this independent review is to provide candid and critical comments that will assist the institution in making its published report as sound as possible and to ensure that the report meets institutional standards for objectivity, evidence, and responsiveness to the study charge. The review comments and draft manuscript remain confidential to protect the integrity of the deliberative process. We wish to thank the following individuals for their review of this report:

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Although the reviewers listed above have provided many constructive comments and suggestions, they were not asked to endorse the conclusions or recommendations nor did they see the final draft of the report before its release. The review of this report was overseen by John Bailar, University of Chicago, (report review monitor) and Andrew Solow, Woods Hole Oceanographic Institution, (report review coordinator). Appointed by the National Research Council, they were responsible for making certain that an independent examination of this report was carried out in accordance with institutional procedures and that all review comments were carefully considered. Responsibility for the final content of this report rests entirely with the authoring committee and the institution.

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Preface

In the 1970s scientists began to realize that a significant quantity of pollutants were being discharged into marine waters worldwide, but very little quantitative data on the volume of discharges were available. Realizing the potential danger to sensitive estuarine and marine habitats, the NRC organized a workshop in 1973, bringing together scientists from a variety of backgrounds to address the problem of petroleum hydrocarbon discharge into the marine environment. This workshop culminated in a report in 1975 by the National Research Council entitled *Petroleum in the Marine Environment*. One of the major findings of the report was recognition that there was a significant lack of systematic data concerning petroleum hydrocarbon discharges. The report, lacking significant quantitative data, was based on estimates and in some instances, educated guesses. Even though lacking substantial quantitative data, the report generated considerable interest and was well-received by industry, government agencies, and scientists. Ten years later, the U.S. Coast Guard requested that the Ocean Sciences Board of the National Research Council update this report, using data that had been acquired in the preceding ten years. Forty-six experts were invited to prepare summary reports on all aspects of petroleum hydrocarbon discharges into the marine environment and to evaluate the fates and effects of these discharges. The resulting report, entitled *Oil in the Sea: Inputs, Fates and Effects*, was published in 1985. This report has served as the seminal publication documenting petroleum pollution in the world's oceans.

Realizing that a considerable amount of data had been accumulated in the past fifteen years, the Minerals Management Service (MMS) approached the Ocean Studies Board to undertake an update of the 1985 report. Financial support was obtained from the Minerals Management Service, the U.S. Geological Survey, the Department of Energy, the Environmental Protection Agency, National Oceanic and Atmospheric Administration, the U.S. Coast Guard, the U.S. Navy, the American Petroleum Institute, and the National Ocean Industries Association.

A committee of fourteen scientists and engineers, representing a wide range of technical backgrounds, was appointed by the National Research Council to prepare the requested report. In addition to simply acquiring and analyzing the data, the committee was charged to document the methodology utilized in preparing the calculated discharges and to verify the databases acquired. This report, hopefully, will serve as a baseline and guide for future studies. It is the committee's opinion that the inputs computed are based on the latest analysis techniques and utilized the best quantitative data available from a wide-range of existing databases. Even though direct comparisons with the earlier reports are difficult to ascertain because of use of differing computational techniques, it is apparent that even though some sources of inputs have decreased in the twenty-year period, discharges from land-based sources, two-stroke engines, and tank vessel spills still represent a considerable volume of discharge of petroleum hydrocarbons into the sea. These discharges are released directly into the ecologically sensitive coastal estuarine environments and are a major concern. It is hoped that this report will help bring attention to this issue and encourage policymakers to explore a variety of options for reducing these discharges.

I wish to thank the committee members for their dedication and hard work during the preparation of the report. Their insistence on maintaining a high level of quality throughout the analysis and interpretation process has resulted in what I believe is a scientifically sound report. The Study Director, Dr. Dan Walker, did an outstanding job of steering the committee to maintain focus on the statement of tasks, insisting on staying on schedule, and providing a balanced approach to the final report. I would like to personally thank him for his professionalism. I would also like to thank Dr. Jennifer Merrill, who worked closely with and guided the committee

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members that compiled the section on the ecological effects of petroleum hydrocarbon discharges. I did not have the background to evaluate this part of the report and her experience and knowledge relieved me of that burden. Also deserving much thanks and recognition are Drs. Laurel Saito, of University of Nevada-Reno, and Dagmar Schmidt Etkin, of Environmental Research, Inc., both of whom worked extensively to develop much of the raw data used to estimate the input of petroleum to the marine environment. The committee members wish to especially thank the hard-working staff, Ms. Megan Kelly, Mrs. Denise Greene, and especially Ms. Julie Pulley, whose hard work greatly helped the committee develop what I think is a high quality final report. Even though the committee and staff had widely varying scientific and working backgrounds, the compilation of the report proved to be a learning experience for all and most of all, an enjoyable experience.

The sponsors are to be commended for their vision in providing funding for this study—a study that could lead to a realization that marine pollution by petroleum hydrocarbons is still a major threat to the marine environment and that future reduction of such discharges should be made a priority of our nation.

James C. Coleman, *Chair*

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Executive Summary

There is little argument that liquid petroleum (crude oil and the products refined from it) plays a pervasive role in modern society. As recently as the late 1990s, the average price of a barrel of crude oil was less than that of a take-out dinner. Yet a fluctuation of 20 or 30 percent in that price can influence automotive sales, holiday travel decisions, interest rates, stock market trends, and the gross national product of industrialized nations, whether they are net exporters or importers of crude oil. A quick examination of world history over the last century would reveal the fundamental impact access to crude oil has had on the geopolitical landscape. Fortunes are made and lost over it; wars have been fought over it. Yet its sheer magnitude makes understanding the true extent of the role of petroleum in society difficult to grasp. Furthermore, widespread use of any substance will inevitably result in intentional and accidental releases to the environment. The frequency, size, and environmental consequences of such releases play a key role in determining the extent of steps taken to limit their occurrence or the extent and nature of mitigation efforts taken to minimize the damage they cause.

Consequently, the United States and other nations engaged in strategic decisionmaking regarding energy use spend a significant amount of time examining policies affecting the extraction, transportation, and consumption of petroleum. In addition to the geopolitical aspects of energy policymaking, the economic growth spurred by inexpensive fuel costs must be balanced against the environmental consequences associated with widespread use of petroleum. Petroleum poses a range of environmental risks when released into the environment (whether as catastrophic spills or chronic discharges). In addition to physical impacts of large spills, the toxicity of many of the individual compounds contained in petroleum is significant, and even small releases can kill or damage organisms from the cellular- to the population-level. Compounds such as polycyclic aromatic hydrocarbons (PAH) are known human carcinogens and occur in varying proportions in crude oil and refined products. Making informed decisions about ways to minimize risks to the environment requires an understanding of how releases of petroleum associated with different components of petroleum extraction, transportation, and consumption vary in size, frequency, and environmental impact.

In recognition of the need for periodic examinations of the nature and effect of petroleum releases to the environment, various governments have commissioned a variety of studies of the problem over the last few decades. Within the United States, federal agencies have turned to the National Research Council on several instances to look at the issue. One of the most widely quoted studies of this type was completed in 1985 and entitled *Oil in the Sea: Inputs, Fates, and Effects*. The report that follows was initially requested by the Minerals Management Service (U.S.) in 1998. Financial support was obtained from the Minerals Management Service, the U.S. Geological Survey, the Department of Energy, the Environmental Protection Agency, National Oceanic and Atmospheric Administration, the U.S. Coast Guard, the U.S. Navy, the American Petroleum Institute, and the National Ocean Industries Association. Although originally envisioned as an update of the 1985 report, this study goes well beyond that effort in terms of proposing a clear methodology for determining estimates of petroleum inputs to the marine environment. In addition, the geographic and temporal variability in those inputs and the significance of those inputs in terms of their effect on the marine environment are more fully explored. Like the 1985 report, this report covers theoretical aspects of the fate and effect of petroleum in the marine environment. This current effort, however, benefited tremendously by the existence of more systematic databases and the voluminous field and laboratory work completed since the early 1980s, work largely stimulated by the *Exxon Valdez* oil spill in Prince William Sound, Alaska.

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PETROLEUM INPUTS TO THE SEA

An examination of reports from a variety of sources, including industry, government, and academic sources, indicate that although the sources of petroleum input to the sea are diverse, they can be categorized effectively into four major groups, natural seeps, petroleum extraction, petroleum transportation, and petroleum consumption. **Natural seeps** are purely natural phenomena that occur when crude oil seeps from the geologic strata beneath the seafloor to the overlying water column. Recognized by geologists for decades as indicating the existence of potentially economic reserves of petroleum, these seeps release vast amounts of crude oil annually. Yet these large volumes are released at a rate low enough that the surrounding ecosystem can adapt and even thrive in their presence. **Petroleum extraction** can result in releases of both crude oil and refined products as a result of human activities associated with efforts to explore for and produce petroleum. The nature and size of these releases is highly variable, but is restricted to areas where active oil and gas exploration and development are under way. **Petroleum transportation** can result in releases of dramatically varying sizes, from major spills associated with tanker accidents such as the *Exxon Valdez*, to relatively small operational releases that occur regularly. **Petroleum consumption** can result in releases as variable as the activities that consume petroleum. Yet, these typically small but frequent and widespread releases contribute the overwhelming majority of the petroleum that enters the sea due to human activity.

Based on analysis of data from a wide variety of sources, it appears that collectively these four categories of sources add, each year on average, about 260,000 metric tonnes (about 76,000,000 gallons) of petroleum to the waters off North America. Annual worldwide estimates of petroleum input to the sea exceed 1,300,000 metric tonnes (about 380,000,000 gallons). Although these are imposing figures, they are difficult to interpret in terms of their ecological significance, as they represent thousands or tens of thousands of individual releases whose combined effect on the environment is difficult to clearly establish. Regional or worldwide estimates of petroleum entering the environment are useful only as a first order approximation of need for concern. Sources of frequent, large releases are rightfully recognized as areas where greater effort to reduce petroleum pollution should be concentrated, despite the fact that not every spill of equal size leads to the same environmental impact. This study, as did the 1975 and 1985 NRC reports, attempts to develop a sense of what the major sources of petroleum entering the marine environment are, and whether these sources or the volume they introduce, have changed through time. Thus, this report not only attempts to quantify the amount released each year, but makes an effort to examine the geographic distribution and nature of releases of petroleum to the marine environment, as well as the processes that can mitigate or exacerbate the effect of these releases on the environment. Where appropriate, comparisons of estimates of petroleum pollution among studies over the last 25 years provide the basis needed to explore the performance for prevention efforts implemented during that time.

Natural Seeps

Natural seepage of crude oil from geologic formations below the seafloor to the marine environment off North America is estimated to exceed 160,000 tonnes (47,000,000 gallons), and 600,000 tonnes (180,000,000 gallons) globally, each year. Natural processes are therefore, responsible for over 60 percent of the petroleum entering North American waters, and over 45 percent of the petroleum entering the marine environment worldwide. Oil and gas extraction activities are often concentrated in regions where seeps form. Historically, slicks of oil from seeps have been attributed to releases from oil and gas platforms, and vice versa. In North America, the largest and best known natural seeps appear to be restricted to the Gulf of Mexico and the waters off of southern California, regions that also have extensive oil and gas production. As mentioned earlier, the seepage of crude oil to the environment tends to occur sporadically and at low rates. **Federal agencies, especially USGS, MMS, and NOAA, should work to develop more accurate techniques for estimating inputs from natural seeps, especially those adjacent to sensitive habitats.** This effort will aid in distinguishing the effects of petroleum released by natural processes versus anthropogenic activities. Furthermore, areas surrounding natural seeps are extremely important natural laboratories for understanding crude oil behavior in the marine environment, as well as how marine life responds to the introduction of petroleum. **Federal agencies, especially USGS, MMS, NSF, and NOAA, should work with industry and the academic community to develop and implement a program to understand the fate of petroleum released from natural seeps and the ecological response to these natural releases.**

Petroleum Extraction

Activities associated with oil and gas exploration or production introduce, on average, an estimated 3,000 tonnes (880,000 gallons) of petroleum to North American waters, and 38,000 tonnes (11,000,000 gallons) worldwide, each year. Releases due to these activities, therefore, make up roughly 3 percent of the total petroleum input by anthropogenic activities to North American waters and 5 percent of the total worldwide. Although dwarfed by some other sources of petroleum to the marine environment, these inputs are not trivial, as they can occur as large spills or as slow, chronic releases concentrated in production fields. Furthermore, those releases from petroleum extraction activities that take place near shore or even on shore can pose

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significant risks to sensitive coastal environments. Again, these releases are concentrated in areas of petroleum production in the Gulf of Mexico and the waters off of southern California, northern Alaska, and eastern Canada. Releases from oil and gas extraction can include accidental spills of crude oil from blow outs, surface spills of crude from platforms, or slow chronic releases associated with the disposal of water produced from oil or gas-bearing formations during extraction (referred to as produced water) or oil-bearing cuttings created during the drilling process. Volatile organic compounds (VOC) commonly associated with, or dissolved in, petroleum are released during extraction activities and also contribute to the total load of hydrocarbon input to the sea. These compounds, however, rapidly volatilize into the atmosphere and thus appear to have a short residence time in marine waters. Despite recent and significant decreases in the amount of petroleum released during extraction activities, the potential for a significant spill, especially in older production fields with aging infrastructures, cannot be ignored. The threat posed by even a minor spill in a sensitive area remains significant. **Federal agencies, especially MMS, should continue to work with state environmental agencies and industry to enhance efforts to promote extraction techniques that minimize accidental or intentional releases of petroleum to the environment.** Furthermore, like areas surrounding natural seeps, production fields represent unique opportunities to study the ecological response to slow, but chronic releases of small amounts of petroleum over time. **Federal agencies, especially USGS, MMS, NSF, and NOAA, should work with industry and the academic community to develop and implement a program to understand the ecological response to such extraction-related releases as part of a larger effort to understand the impact of chronic releases from all sources of petroleum to the marine environment.**

Petroleum Transportation

The transportation (including refining and distribution activities) of crude oil or refined products results in the release, on average, of an estimated 9,100 tonnes (2,700,000 gallons) of petroleum to North American waters, and 150,000 tonnes (44,000,000 gallons) worldwide, each year. Releases due to the transportation of petroleum, therefore, make up roughly 9 percent of the total petroleum input through anthropogenic activities to North American waters and less than 22 percent worldwide. Similar to releases from petroleum extraction, these volumes are dwarfed by those from other sources of petroleum to the marine environment. And like releases from extraction activities, these inputs are not trivial, as they can occur as large spills. Unlike releases associated with extraction, which tend to be concentrated in production fields in the Gulf of Mexico or coastal areas off California and Alaska, these spills can occur anywhere tanker vessels may travel or where pipelines are located statistically. Areas near major petroleum handling facilities face the greatest threat. Spills from transportation activities may release a wide variety of petroleum products (not just crude oil) each of which behaves differently in the environment (for example light distillates tend to evaporate rapidly), or contain different concentrations of toxic compounds like PAH. VOC are also released from tankers underway or involved in loading and offloading activities, and they contribute to the total load of hydrocarbons input to the sea. Again, these compounds rapidly volatilize into the atmosphere and thus appear to have a short residence time in marine waters. Despite recent and substantive decreases in the size and frequency of petroleum spills from tankers, the potential for a large spill is significant, especially in regions without stringent safety procedures and maritime inspection practices. Furthermore, tanker traffic is expected to grow over the coming decades as the centers of oil production continue to migrate towards the Middle East and Russia. **Federal agencies, such as the U.S. Coast Guard and the Maritime Administration, should expand efforts to work with ship owners domestically and internationally through the International Maritime Organization, to develop and enforce effective international regulatory standards that have contributed to the decline in oil spills and operational discharges.** In addition, the potential for large spills from aging pipelines and other coastal facilities is especially disconcerting, as these facilities often lie near sensitive coastal areas. **Federal agencies, especially the U.S. Coast Guard, the Office of Pipeline Safety, and EPA, should continue to work with state environmental agencies and industry to evaluate the threat posed by aging pipelines and to take steps to minimize the potential for a significant spill.**

Petroleum Consumption

Releases that occur during the consumption of petroleum, whether by individual car and boat owners, non-tank vessels, or runoff from increasingly paved urban areas, contribute the vast majority of petroleum introduced to the environment through human activity. On average, an estimated 84,000 tonnes (25,000,000 gallons) of petroleum are input to North American waters, and 480,000 tonnes (140,000,000 gallons) are input worldwide, each year from these diffuse sources. **Therefore, releases associated with the consumption of petroleum make up nearly 70 percent of the petroleum introduced to the world's oceans from anthropogenic sources and nearly 85 percent of the total petroleum input from anthropogenic sources to North American waters.** Unlike other sources, inputs from consumption occur almost exclusively as slow, chronic releases. Furthermore, because the vast majority of the consumption of petroleum occurs on land, rivers and waste- and stormwater streams represent the most significant source of petroleum to the marine environment. Another smaller, but still

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significant source, are two-stroke engines. Collectively, land runoff and two-stroke engines account for nearly three quarters of the petroleum introduced to North American waters from activities associated with petroleum consumption. This is particularly significant because, by their very nature, these activities are almost exclusively restricted to coastal waters. In fact, the estuaries and bays that receive the bulk of the load are often some of the most sensitive ecological areas along the coast. **Federal agencies, especially EPA, should continue efforts to regulate and encourage the phase-out of older, inefficient two-stroke engines, and a coordinated enforcement policy should be established.** Unfortunately, the estimates for land-based sources of petroleum are the most poorly documented, and the uncertainty associated with the estimates range over several orders of magnitude. **Federal agencies, especially EPA, USGS, and NOAA, should work with state and local environmental agencies to develop and implement a system for monitoring the input of petroleum to the marine environment from land-based sources via rivers and storm- and waste-water facilities.** Again, VOC are released during consumption activities and contribute to the total load of hydrocarbon input to the sea. Like VOC released by other sources, these compounds rapidly volatilize into the atmosphere and thus appear to have a short residence time in marine waters.

Significant Cross-cutting Issues

As discussed briefly above, the effect of a release of petroleum is not directly related to the volume. It is instead a complex function of the rate of release, the nature of the released petroleum (and the proportions of toxic compounds it may contain), and the local physical and biological ecosystem exposed. Progress has been made in understanding some basic processes affecting the fate of released petroleum. Much more needs to be learned about how petroleum interacts with marine sediment and how it is transported or dispersed by ocean and coastal processes such as waves and currents. **Federal agencies, especially NOAA, MMS, U.S. Coast Guard, and the USGS, should work with industry to develop and support a systematic and sustained research effort to further basic understanding of the processes that govern the fate and transport of petroleum hydrocarbons in the marine environment.**

Although the VOC released during the extraction, transportation, and consumption of petroleum appear to have short residence times in the marine environment, their impact on air quality may be significant. **Federal agencies, especially the U.S. Coast Guard, MMS, and EPA, should work with the International Maritime Organization to assess the overall impact of VOC on air quality from tank vessels and other sources, and establish design and/or operational standards on VOC emissions where appropriate.**

Studies completed in the last 20 years again bear out the significant environmental damage that can be caused by spills of petroleum into the marine environment. No spill is entirely benign. Even a small spill at the wrong place, at the wrong time, can result in significant damage to individual organisms or entire populations. With a few notable exceptions (e.g., the *Exxon Valdez*, *North Cape*, and Panama spills), there have been a lack of resources to support studies of the fates and effects of spilled oil. Much of what is known about the fate and effect of spilled oil has been derived from a very few, well-studied spills. **Federal agencies, especially the U.S. Coast Guard, NOAA, and EPA, should work with industry to develop and implement a rapid response system to collect in situ information about spill behavior and impacts.**

Despite the significant progress made in understanding the behavior and effect of petroleum spills on the marine environment and on preventing their occurrence in the first place, relatively little work has progressed on understanding the threat posed by small, chronic releases of petroleum from all sources. Insights have been made from long-term studies of sites of major spills or polluted harbors, but to a large degree the significance (in terms of environmental damage) of the large inputs from land-based sources or other chronic releases is not known. Recent studies, however, suggest that PAH, even in low concentrations, can have a deleterious effect on marine biota. Furthermore, research on the cumulative effects of multiple types of hydrocarbons in combination with other types of pollutants is needed to assess toxicity and organism response under conditions experienced by organisms in polluted coastal zones. **Federal agencies, especially EPA, NOAA, NSF, USGS, and MMS, should work with academia and industry to develop and implement a major research effort to more fully understand and evaluate the risk posed to the marine environment by the chronic release of petroleum (especially the cumulative effects of multiple types of hydrocarbons present in these kinds of releases).**

Finally, although there is now good evidence for the toxic effects of oil pollution on individual organisms and on the species composition of communities, there is little information on the effects of either acute or chronic oil pollution on populations or on the function of communities or ecosystems. The lack of understanding of population-level effects lies partly in the fact that the structure of populations of most marine organisms is poorly known. Such information is imperative if the impacts of individual spills or chronic releases in local areas are to be evaluated against the health of entire populations, species, or ecosystems. **The U.S. Departments of Interior and Commerce should identify an agency, or combination of agencies, to prioritize and support continued research on the effects of releases (chronic and catastrophic) of petroleum on wild populations.**

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I

Introduction and Overview

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1

Introduction

In August of 1859, Colonel Drake drilled a well to a depth of 70 feet in Titusville, Pennsylvania, and discovered oil—an event that has changed the world. During the late 1800s, a number of small wells were drilled in Pennsylvania, Kentucky, and California, but the well that is generally credited with giving "birth to the modern oil industry" was the discovery at Spindletop in 1901 atop a salt dome near Beaumont, Texas (Knowles, 1983). From that time on, the nation's, and indeed the world's, demand for fossil fuel has continuously increased. Petroleum hydrocarbon extraction, transportation (pre- and post-refining), refining, and consumption by industry and the public account for a high percentage of the U.S. economy. Oil and natural gas are the dominant fuels in the U.S. economy, providing 62 percent of the nation's energy and almost 100 percent of its transportation fuels (National Energy Policy Development Group, 2001). Similar trends are also present in many other nations. Expanding global economies, population increases, and a worldwide improvement in the standard of living have resulted in this increasing quest for fossil fuel. By the year 2020, the United States will need about 50 percent more natural gas and one-third more oil to meet the energy demands of a growing population (National Energy Policy Development Group, 2001). (While this trend is expected to continue in future years, it is subject to change based on future world geopolitical developments.) Liquid petroleum is the nation's largest source of primary energy, accounting for approximately 40 percent of U.S. energy needs. In transportation alone the United States consumed an average of 19.5 million barrels (2.8 million tonnes[1]) of oil every day in 2000, compared to 9.8 million barrels per day (mb/d; 1.4 million tonnes per day; mt/d) in 1960; transportation fuels account for approximately 66 percent, the industrial sector accounts for 25 percent, and residential and commercial uses represent most of the remainder (National Energy Policy Development Group, 2001).

Energy intensity, the amount of energy it takes to produce a dollar of gross domestic product (GDP), has declined steadily in the United States over the last 30 years. This decline is due to improvements in energy efficiency, as well as a shift from manufacturing to services. However, the rise in GDP has outpaced the declining energy intensity, resulting in an overall increase in energy consumption.

Such widespread use, however, of any substance will inevitably lead to accidental and intentional releases. Liquid petroleum, whether crude oil or refined products such as tar, lubricating oil, gasoline, or kerosene, possesses many properties and contains many individual toxic compounds that can make such releases harmful to the environment. Thoughtful decisionmaking about the extent of petroleum extraction and use must therefore include a thorough understanding of the potential nature, location, and frequency of releases and the ecological risk they pose the environment.

ENERGY NEEDS OF THE NATION

Nearly 30 years have passed since the Arab oil embargo disrupted the U.S. oil supply, and at the time of the embargo, domestic oil production was in the middle of a 7-year decline (Riva, 1995). Our nation's prosperity and way of life are sustained by energy use. Estimates indicate that over the next 20 years, U.S. oil consumption will increase by 33 percent, natural gas consumption by well over 50 percent, and the demand for electricity by 45 percent (National Energy Policy Development Group, 2001). Major reasons for this increased demand for energy have been a growing population and heavy increases in fuel for transportation. Table 1-1 shows the consumption of petroleum by end-use sector for 1973-1999. Whereas residential, commercial, and electric

[1]On average, 42 U.S. gallons equal 1 barrel, and seven barrels equal roughly one metric ton (tonne) of crude oil. U.S. production and consumption figures are often discussed in barrels and gallons rather than in tonnes; thus, the text in this chapter makes use of all three units as appropriate.

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TABLE 1-1 Consumption of Petroleum by End-Use Sector, 1973-1999 (quadrillion Btu)

Year	Transportation	Percentage	Residential & Commercial	Percentage	Industrial	Percentage	Electric Utilities	Percentage	Total
1973	17.83	51.2	4.39	12.6	9.1	26.1	3.52	10.1	34.84
1974	17.4	52.0	4	12.0	8.69	26.0	3.37	10.1	33.46
1975	17.61	53.8	3.81	11.6	8.15	24.9	3.17	9.7	32.74
1976	18.51	52.6	4.18	11.9	9.01	25.6	3.48	9.9	35.18
1977	19.24	51.8	4.21	11.3	9.77	26.3	3.9	10.5	37.12
1978	20.04	52.8	4.07	10.7	9.87	26.0	3.99	10.5	37.97
1979	19.83	53.4	3.45	9.3	10.57	28.5	3.28	8.8	37.13
1980	19.01	55.6	3.04	8.9	9.53	27.9	2.63	7.7	34.21
1981	18.81	58.9	2.63	8.2	8.29	26.0	2.2	6.9	31.93
1982	18.42	60.9	2.45	8.1	7.79	25.8	1.57	5.2	30.23
1983	18.59	61.9	2.5	8.3	7.42	24.7	1.54	5.1	30.05
1984	19.22	61.9	2.54	8.2	8.01	25.8	1.29	4.2	31.06
1985	19.5	63.1	2.52	8.2	7.81	25.3	1.09	3.5	30.92
1986	20.27	63.0	2.56	8.0	7.92	24.6	1.45	4.5	32.2
1987	20.87	63.5	2.59	7.9	8.15	24.8	1.26	3.8	32.87
1988	21.63	63.2	2.6	7.6	8.43	24.6	1.56	4.6	34.22
1989	21.87	63.9	2.53	7.4	8.13	23.8	1.69	4.9	34.22
1990	21.81	65.0	2.17	6.5	8.32	24.8	1.25	3.7	33.55
1991	21.46	65.3	2.15	6.5	8.06	24.5	1.18	3.6	32.85
1992	21.81	65.0	2.13	6.4	8.64	25.8	0.95	2.8	33.53
1993	22.2	65.6	2.14	6.3	8.45	25.0	1.05	3.1	33.84
1994	22.76	65.6	2.09	6.0	8.85	25.5	0.97	2.8	34.67
1995	23.2	67.1	2.08	6.0	8.62	24.9	0.66	1.9	34.56
1996	23.74	66.4	2.2	6.2	9.1	25.4	0.73	2.0	35.77
1997	24	66.2	2.14	5.9	9.31	25.7	0.82	2.3	36.27
1988	24.64	66.7	1.97	5.3	9.15	24.8	1.17	3.2	36.93
1999	25.21	66.9	2.07	5.5	9.45	25.1	0.97	2.6	37.7

SOURCE: U.S. Department of Energy, Energy Information Administration, *Monthly Energy Review, March 2000*, pp. 27, 29, 31, 33.

utilities consumption has decreased, and industrial consumption has remained nearly constant, consumption by transportation has increased substantially.

The U.S. population has increased from 180.7 million to 272.7 million in the past 40 years, an increase of 92 million people. Figure 1-1 illustrates U.S. oil production and consumption for 1960 through 1997 (Davis, 2000). Consumption increased from 9.8 mb/d (1.4 mt/d) in 1960 to 18.6 (2.8 mt/d) mb/d in 1997, an increase of 8.8 mb/d, and it has continued to increase during the past decade. U.S. oil production, however, has remained rather constant and since 1985 has been declining (Figure 1-1). As a result, U.S. consumption is presently nearly three times U.S. production. Figures 1-2 and 1-3 illustrate projections of consumption and production of oil and natural gas in the United States for the next 20 years (National Energy Policy Development Group, 2001). Note that oil consumption will exceed production by 19 mb/d (2.7 mt/d) in the year 2020, and natural gas consumption will exceed production by 13.5 trillion cubic feet in the same time. Today, the United States produces 39 percent less oil than it did in 1970, leaving us ever more reliant on foreign suppliers. As consumption increases and production decreases, net imports will have to increase to meet this demand (Figure 1-4). The United States has been a net importer of oil since the 1950s, and today oil accounts for 89 percent of net U.S. energy imports (National Energy Policy Development Group, 2001). If the projections of oil consumption are correct, the United States will have to import nearly 20 mb/d (2.9 mt/d) by the year 2020—double its current amount.

WORLD ENERGY NEEDS AND RESOURCE AVAILABILITY

As the population of the world increases and developing nations become more industrialized, the demand for energy will increase. Oil is currently the dominant energy fuel and is expected to remain so over the next several decades (see Figure 1-5). There is general agreement that the availability of oil will not be a significant constraint on oil demand through 2020, because the reserve-to-production ratio for Persian Gulf producers currently exceeds 85 years. Worldwide petroleum consumption is projected to increase by 44.7 mb/d (6.4 mt/d), from 74.9 mb/d (10.7 mt/d) in 1999 to 119.6

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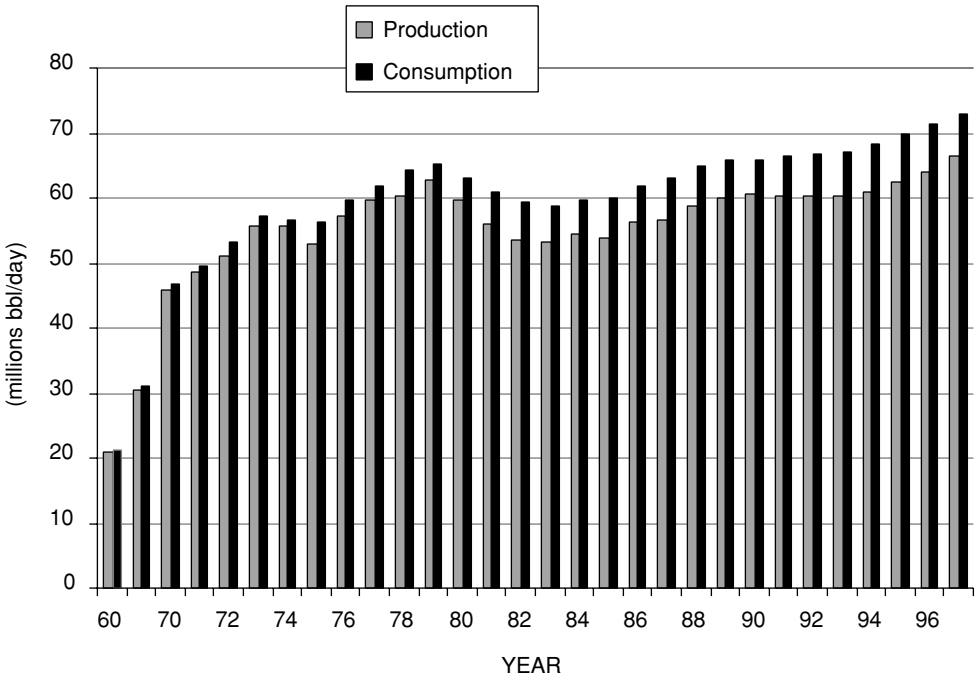

FIGURE 1-1 Worldwide petroleum production and consumption 1960-1997 (data from Davis, 2000).

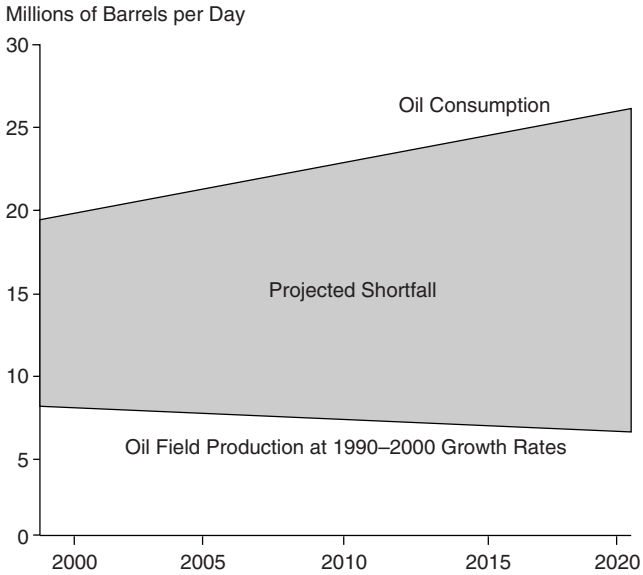

FIGURE 1-2 Projected oil field U.S. production (millions of barrels per day) at 1990-2000 growth rates (Energy Information Administration, 2000; National Energy Policy Group, 2001).

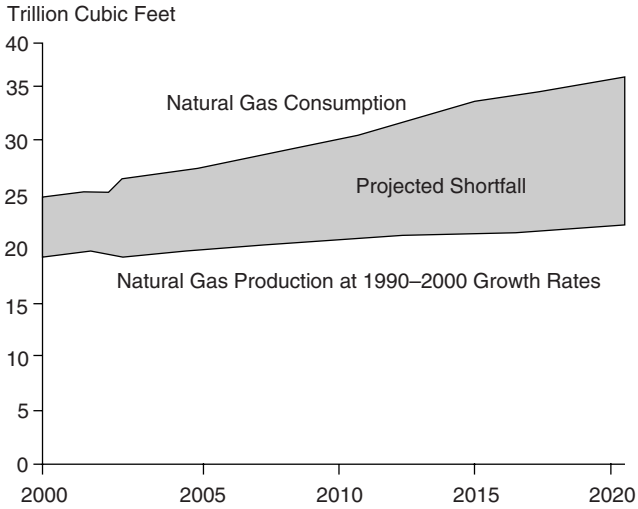

FIGURE 1-3 Projected natural gas U.S. production (trillion cubic feet) at 1990-2000 growth rates (Energy Information Administration, 2000; National Energy Policy Group, 2001).

mb/d (17 mt/d) in 2020. The annual rate of growth is projected at 2.3 percent, as compared to a growth rate of 1.6 percent per year from 1970 to 1999.

Historically, the industrialized nations have been the major consumers of oil (see Figure 1-6). However, by the year 2020, consumption in the developing countries is expected to be nearly equal to that of the industrialized countries. The largest growth in oil demand over the next two decades is projected for the developing countries of Asia. In particular, from 1999 to 2020 the oil demands of China and India are projected to increase by 6.1 mb/d (0.9 mt/d) and 3.9 mb/d (0.6 mt/d), respectively. The majority of this expected in-

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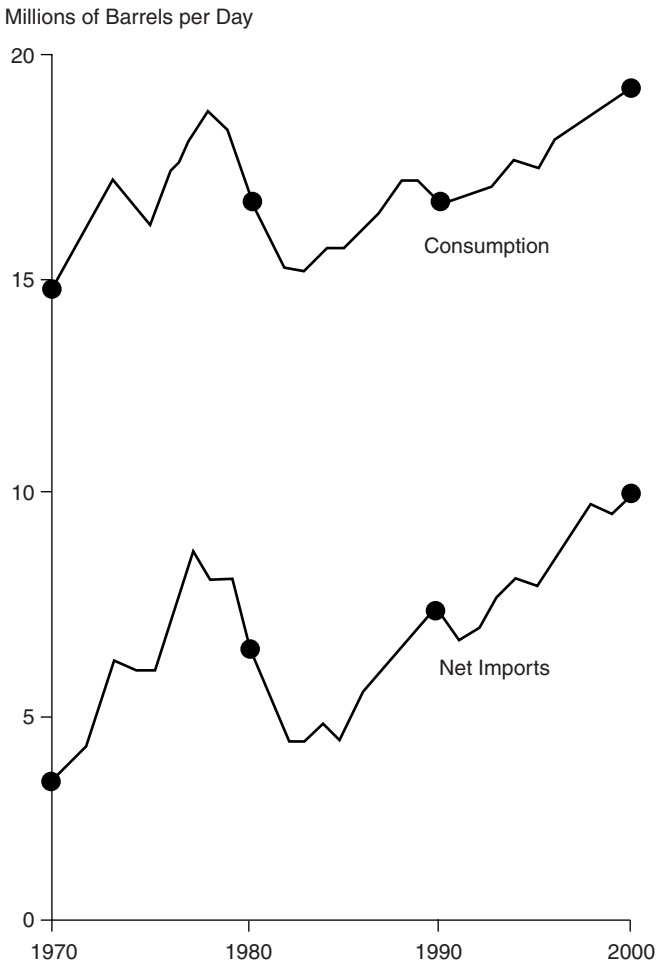

FIGURE 1-4 Comparison of historical trends (millions of barrels per day) in U.S. consumption and importation of oil (National Energy Policy Group, 2001).

PHOTO 1 The Genesis Spar, located in the Green Canyon 205 Field about 150 miles south of New Orleans, is typical of the new technology allowing oil and gas development in deep waters of the Gulf of Mexico. (The original discovery well was drilled in 1988 in 2600 feet of water.) The Genesis Development Project is a joint venture development between ChevronTexaco Production Company, Exxon Company USA, and PetroFina Delaware, Inc. (Photo courtesy of Environmental Research Consulting.)

crease is related to the transportation sector and more specifically, to motor vehicles. Significant increases in land-based runoff of petroleum hydrocarbons can be expected as a by-product of this increased consumption.

To meet the increased demand, an increase in world oil supply of roughly 45 mb/d (6.4 mt/d) is projected for the next two decades. It is expected that Organization of the Petroleum Exporting Countries (OPEC) producers will be responsible for more than two-thirds of this increase. Imports into industrialized countries are therefore expected to increase from 34.0 to 43.7 mb/d (4.9 to 6.2 mt/d), and imports into developing countries from 19.3 mb/d to 42.8 mb/d (2.8 to 6 mt/d). Much of these imports will move by sea. Major importers and exporters are shown in Figure 1-7. Increased imports into China and Pacific Rim countries will come largely from the Persian Gulf. North American imports are projected to increase from 11.0 mb/d (1.57 mt/d) in 1998 to about 18.0 mb/d (2.6 mt/d) in 2020. More than half of the North American imports are expected to come from the Atlantic Basin, principally Latin American and West African producers. Imports into North America from the Persian Gulf are expected to double, from 2.2 to 4.2 mb/d (0.3 to 0.6 mt/d).

It is apparent that greater and greater amounts of oil will be transported by vessel, refineries will have to increase capacity, and more coastal petroleum handling facilities will be needed. These have the potential to increase the input of hydrocarbons into the oceans. However, the operational and accidental discharge of oil from vessels and platforms has declined substantially over the past three decades, and it is reasonable to expect continued improvements in these areas in future years as the benefits from recently enacted regulations and improved operational practices are fully realized. The expected growth in worldwide consumption, with much of the increase concentrated in the transportation sector, is of concern. Land-based runoff of petroleum hydrocarbons can

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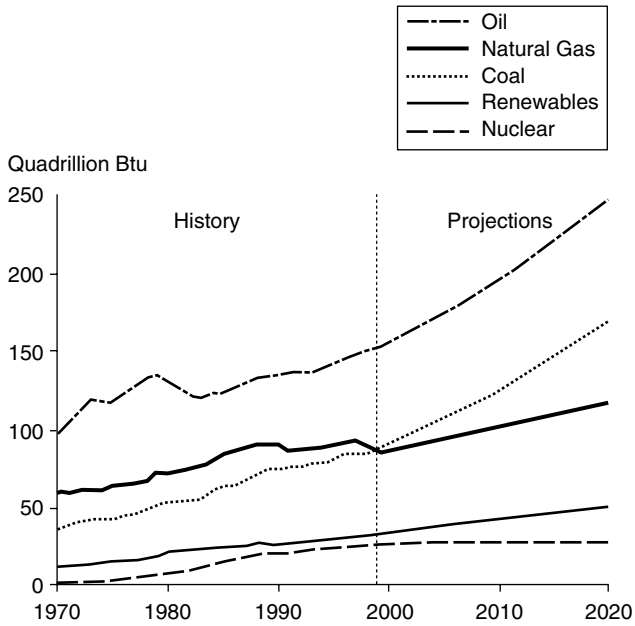

FIGURE 1-5 Worldwide energy consumption by fuel type, 1970-2020 (Energy Information Administration, 1999).

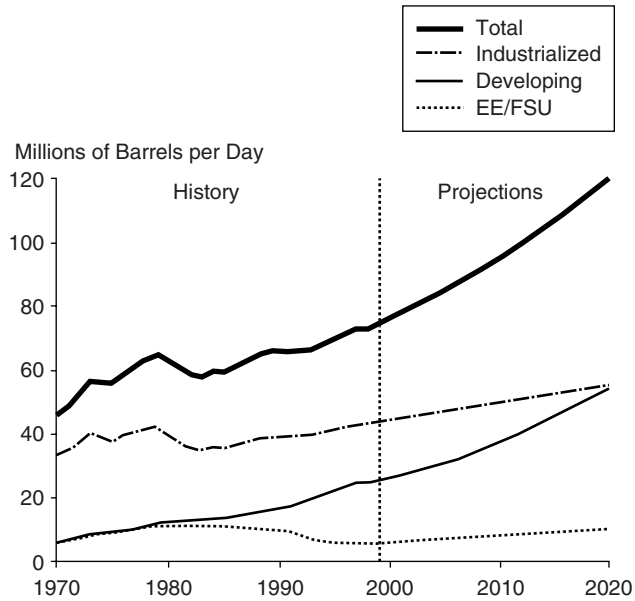

FIGURE 1-6 Worldwide consumption by region, 1970-2020 (Energy Information Administration, 1999).

be expected to increase with consumption unless steps are taken to reduce the release of petroleum from consumption-related activities.

EXXON VALDEZ AS SEMINAL MOMENT

On March 24, 1989, the tanker *Exxon Valdez*, en route from Valdez, Alaska, to Los Angeles, California, ran aground on Bligh Reef in Prince William Sound, Alaska. The vessel was traveling outside normal shipping lanes in an attempt to avoid ice. Within six hours of the grounding, the *Exxon Valdez* spilled approximately 10.9 million gallons (37 kilotonnes) of its 53 million gallon cargo (156 kilotonnes) of North Slope Crude oil. The oil would eventually impact more than 1,100 miles (2400 km) of noncontinuous coastline in Alaska, making it the largest oil spill to date in U.S. waters. The biological consequences of the *Exxon Valdez* oil spill (EVOS) have been well studied, resulting in significant insights and raising important questions about lethal and sublethal impacts of oil exposure (Box 1-1). The scientific controversies arising from work carried out in and around Prince William Sound have important implications for understanding effects from the release of oil at a variety of scales. Thus, while resolving specific controversies centered around EVOS is clearly beyond the scope of the study, they are discussed in terms of their broader implications throughout this report, but especially in Chapters 2 and 5.

The response to the *Exxon Valdez* involved more personnel and equipment over a longer period of time than any other accidental spill in U.S. history. At the height of the response, more than 11,000 personnel, 1,400 vessels, and 85 aircraft were involved in the cleanup. Shoreline cleanup began in April of 1989 and continued until September of 1989 for the first year of the response. The effort continued in 1990 and 1991 with cleanup in the summer months and limited shoreline monitoring in the winter. Monitoring of fate and effects by state and federal agencies continues.

Beyond the ecological damage, the *Exxon Valdez* disaster caused fundamental changes in the way the U.S. public thought about oil, the oil industry, and the transport of petroleum products by tankers. Despite continued heavy use of fossil fuels in nearly every facet of our society, "big oil" was suddenly seen as a necessary evil, something to be feared and mistrusted. The reaction was swift and significant.

PREVIOUS STUDIES

The extraction, transportation, and consumption of petroleum hydrocarbons increased significantly with the expansion of modern ground and air transportation systems and the need for industrial and public power generation. Early in the twentieth century, greater attention was paid simply to the demand for more oil than to the environmental consequences of the potential pollution problems associated with its extraction, transportation, and consumption. Because little was known about petroleum hydrocarbon inputs to the marine environment, a workshop was convened in 1973 to evaluate this aspect of marine pollution. It led to the publication in 1975 of a National Research Council (NRC) report entitled *Petroleum in the Marine Environment*. That report, using the best data available at the time, discussed petroleum hydrocarbon inputs, analytical methods, fates, and effects of oil discharged to the marine environment. The report gener-

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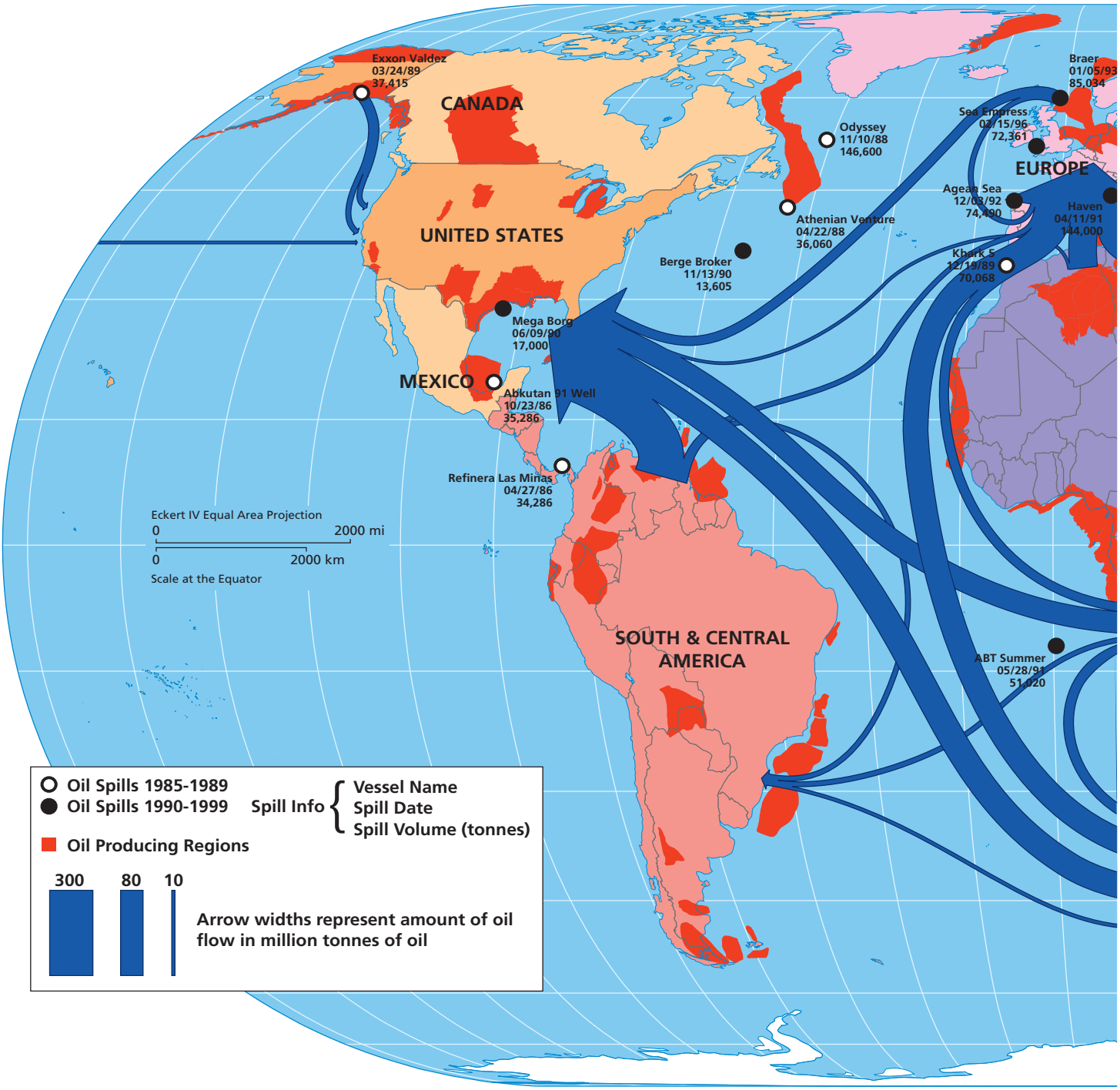

FIGURE 1-7 Worldwide sea borne flow of oil in 2000 (modified from Newton, 2002; other information sources include U.S. Geological Survey, U.S. Coast Guard, Minerals Management Service). Solid black dots indicate spills included in the average, annual (1990-1999) estimates discussed in this report.

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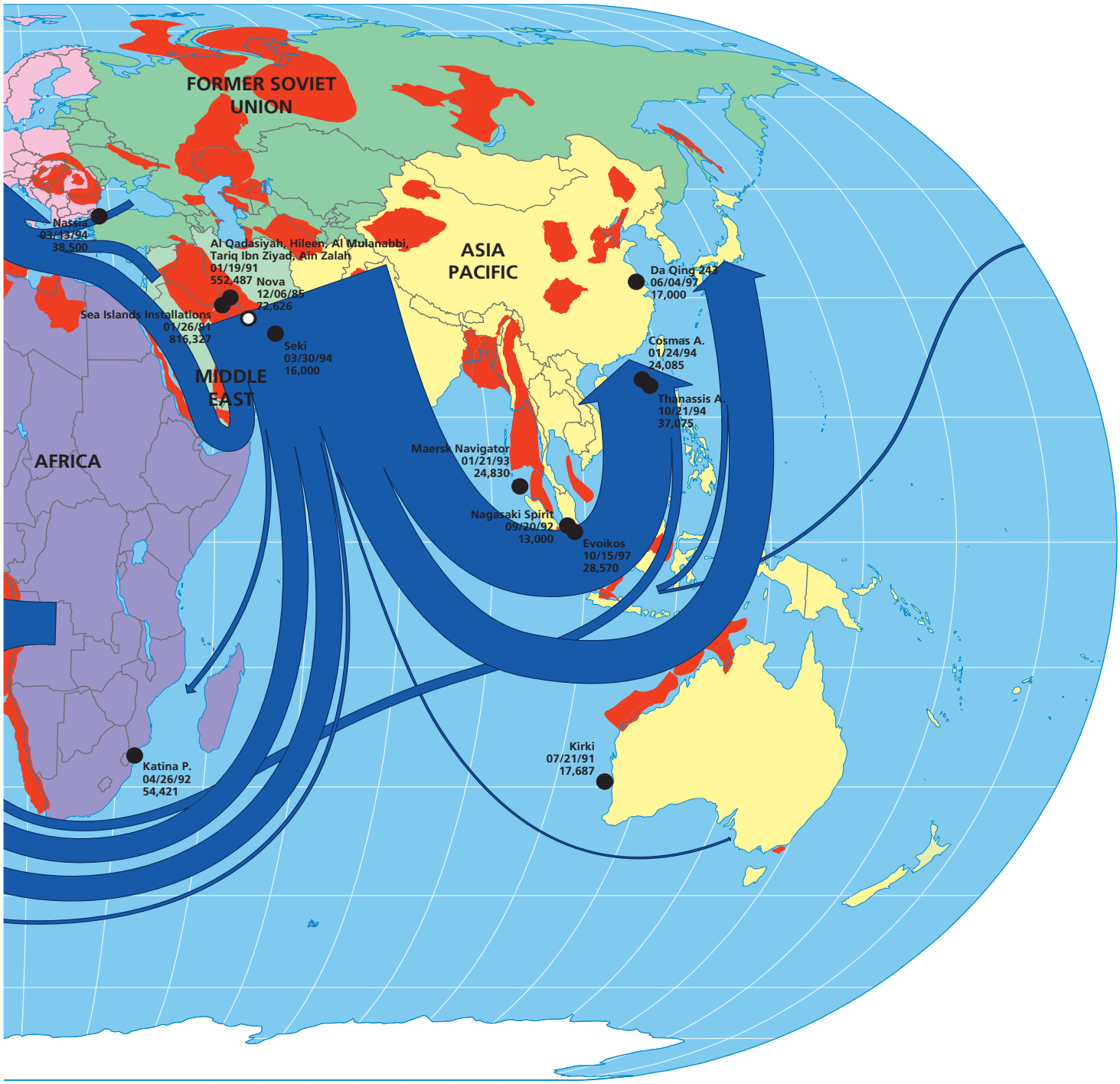

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BOX 1-1
***T/V Exxon Valdez*, Alaska**

The *T/V Exxon Valdez* grounded on Bligh Reef in Prince William Sound, Alaska on March, 24 1989, releasing an estimated 36,000 tonnes (10.9 million gallons) of Alaska North Slope crude oil (API [American Petroleum Institute] gravity = 29.8). Wolfe et al. (1994) estimated that, as of 1991, 41 percent of the oil stranded on intertidal habitats in Prince William Sound. About 25 percent was transported out of the sound, stranding mostly along the Kenai Peninsula, lower Cook Inlet, and the Kodiak Archipelago. More than 2,000 km of shoreline were oiled, reflecting the persistence of the spilled oil and the influence of a spring gale and a major coastal current on the transport of a large volume of oil. The extent and degree of shoreline oiling resulted in the most intensive shoreline cleanup effort ever attempted. Large volumes of water heated to 140°F were used to flush oil from almost 30 percent of the rocky shores and gravel beaches in Prince William Sound. Despite the aggressive cleanup, oil residues persisted for more than 13 years in more sheltered habitats and porous gravel beaches. Monitoring studies have shown that intensive treatment resulted in delayed recovery of rocky shore intertidal communities (NOAA, 1997). These studies demonstrate how too-aggressive cleanup, in some instances, can slow recovery of these affected communities.

No doubt, the *Exxon Valdez* was a large spill that affected many valuable resources. Large numbers of animals were estimated to have been killed directly, including 900 bald eagles (Bowman, 1993), about 250,000 seabirds (Piatt and Ford, 1996), 2,800 sea otters (Garrott et al., 1993; Bodkin et al., 2001), and 300 harbor seals (Frost et al., 1994a). Both the *Exxon Valdez* Oil Spill Trustee Council and Exxon conducted numerous studies to assess the impacts of the spill, and Exxon paid the state and local governments $900 million for natural resource damages. Never before have so much effort and money been spent on trying to determine the extent of negative effects and the course of recovery. Yet the interpretations of the studies conducted by the trustees and Exxon varied significantly, particularly concerning sublethal and long-term impacts. There were issues with the scale and power of the studies, interpretations of uncertainty, the role of natural changes in gauging recovery, and even the source of the background hydrocarbons in Prince William Sound. The trustees' results showed enhanced mortality to pink salmon larvae hatching in oiled gravel beds that affected their productivity and survival (Heintz et al., 1999, 2000). Exxon studies showed equal survival of eggs collected from oiled and unoiled streams (Brannon et al., 1995). Carls et al. (1999) concluded that oil exposure contributed to disease induction that caused a collapse in Pacific herring five years after the spill, although other factors could have played a role. Black oystercatchers and harlequin ducks from oiled areas of western PWS were thought to have significant declines in abundance and productivity for at least four years post-spill for oystercatchers (Klosiewski and Laing, 1994; Andres, 1997) and eight years for harlequin ducks (Esler et al., 2000c) when compared to populations from unoiled eastern PWS, although the number of breeding pairs studied was very small. However, laboratory analyses reported by Boehm et al. (1996) concluded that the body burden for individuals in the PWS duck populations were 1-3 orders of magnitude lower than that shown to cause demonstrable effects in mallards. The *Exxon Valdez* oil spill changed much about what is now done to prevent such spills, to be better prepared for response, and to select shoreline cleanup methods, as well as to understand the acute and long-term impacts of oil on a wide range of species, communities, and habitats.

ated considerable interest and was used as a primary source of information by industry, government agencies, scientists, and the general public. By the mid-1980s, it was realized that an update to this important document was needed, and the U.S. Coast Guard requested that the Ocean Sciences Board of the National Research Council (later the Board on Ocean Science and Policy [BOSP] and now the Ocean Studies Board [OSB]) undertake a new examination of this subject. The BOSP appointed a steering committee consisting of six members from academia, government service, and industry to be responsible for updating the 1975 NRC report. A public meeting was held in 1980, at which representatives from the oil industry, universities, government, and environmental groups were invited to make presentations on topics important to the committee. In early 1981, 46 expert contributors were invited to prepare summary papers on all aspects of petroleum in the world's oceans, and later in 1981, an international workshop was held to discuss the main issues of petroleum hydrocarbon inputs into the marine environment. In early 1982, the steering committee began preparing the new report, which was published in 1985. The report *Oil in the Sea: Inputs, Fates, and Effects* (NRC, 1985) generally followed the same format as the 1975 report but was much more detailed and contained significant new data and information that had been acquired since the earlier report. The 1985 report has served as a seminal publication that documented petroleum hydrocarbon discharge into the marine environment and the fates and effects of this discharge.

Prior to and since the 1985 NRC report *Oil in the Sea*, there have been a series of studies undertaken to examine the load of petroleum hydrocarbons to the marine environment. The majority of studies has focused on quantifying the volume from tanker spills, and many have been conducted under the auspices of the International Maritime Organization (IMO) or its Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP). One of the most recent GESAMP reports, *Impact of Oil and Related Chemicals*

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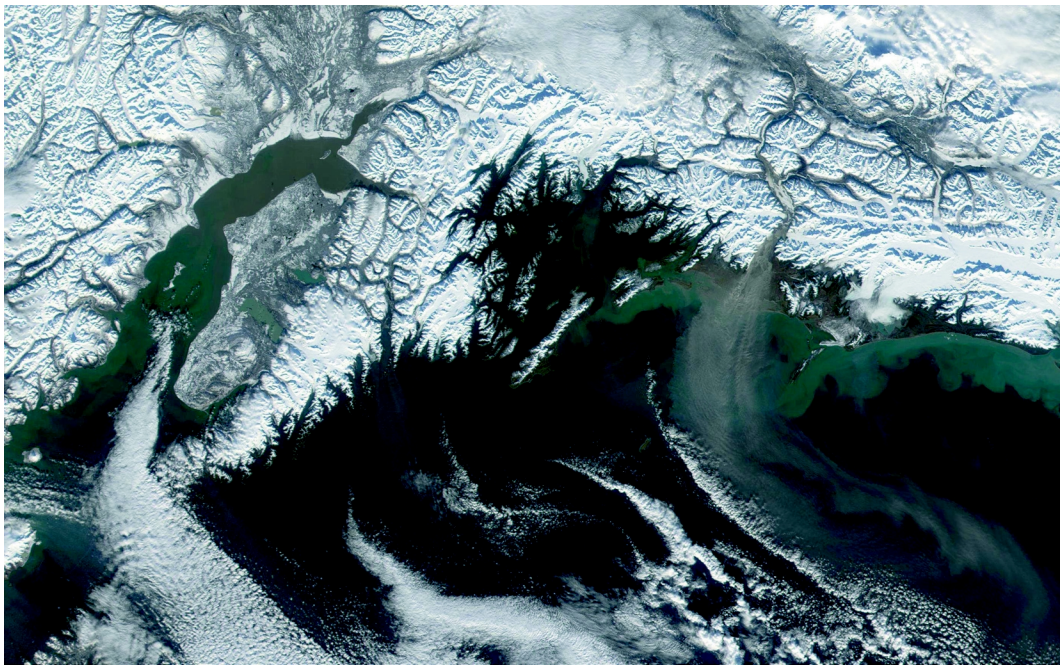

PHOTO 2 MODIS (or Moderate Resolution Imaging Spectroradiometer) satellite imagery (250 m resolution) of southern Alaska, including Cook Inlet (on the left), Prince William Sound (center) and the Copper River delta (on the right). The *Exxon Valdez* ran aground on Bligh Reef in northeastern Prince William Sound on March 24, 1989, eventually releasing 10.9 million gallons of crude oil. (Image courtesy of NASA.)

and Wastes on the Marine Environment (GESAMP, 1993), summarizes studies completed prior to 1993.[2] Table 1-2 was compiled from that report and summarizes estimates of the release of crude oil and refined petroleum products through 1985.

Limitations to Examining Historical Estimates

In addition to the NRC studies discussed above, the 1993 GESAMP report specifically discusses an 1990 update of volumes from maritime operations reported in the 1985 NRC report. The numbers given in the 1993 GESAMP report and listed in Table 1-3 are not official or reviewed estimates, but are based on discussions held at an NRC planning workshop in 1990. Despite the absense of any analysis to determine how changes in data and methods might bring about changes in overall estimates, GESAMP (1993) attributed the reduction from 1.47 million tonnes in 1981 to 0.54 million tonnes to the entry into force of the International Convention for the Prevention of Pollution from Ships (MARPOL 73/78). This analysis points out a significant obstacle that one encounters when trying to draw long-term conclusions about relative changes in estimates from various sources of petroleum to the sea. Lack of rigorous review or thorough documentation of the methods used in each analysis makes comparisons among various studies almost meaningless.

SCOPE OF CURRENT STUDY

In the fall of 1997, representatives of the U.S. Minerals Management Service approached the Ocean Studies Board of the National Research Council (NRC) about officially updating the 1985 NRC report *Oil in the Sea*. After numerous discussions, it was agreed that the primary function of the new study would be not only to develop new estimates for the load of petroleum hydrocarbons to the sea, but also to develop and widely disseminate the methods and sources of data used to derive those estimates. Furthermore, because of the greater availability of data for North American waters, the NRC was asked to evaluate spatial and temporal trends in the release of petroleum hydrocarbons to those waters. Finally, the NRC was asked to review the tremendous number of studies on the fate and effect of petroleum in the marine environment that had been published since the release of *Oil in the Sea* (NRC, 1985) in an effort to drawn some conclusions about the relative threats to the marine environment posed by various sources. (It was agreed early on that inclusion of an examination of potential effects on human

[2]GESAMP is currently attempting to examine the impact of entry into force of MARPOL 73/78 (The International Convention for the Prevention of Pollution from Ships) on tanker spills worldwide. That report is expected to be released in 2002.

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TABLE 1-2 Worldwide Estimates of Total Petroleum Input to the Sea

Summary of Inputs (thousand tonnes × 1000)	NRC, 1975	Kornberg, 1981	Baker, 1983	NRC, 1985
Natural seeps	600	600	300 (50-500)	200 (20-2,000)
Extraction of petroleum	80	60	50 (40-70)	50 (40-60)
Transportation of petroleum	1,580	1,110	1,150	1,250
Pipeline spills[a]				
Spills (tank vessels)	300	300	390 (160-640)	400 (300-400)
Operational discharges (cargo washings)	1,080	600	710 (440-14,500)	700 (400-1,500)
Coastal facility spills	200	60	100 (60-6,000)	
Other coastal effluents	150	50 (30-80)	50 (50-200)	
Consumption of petroleum	3,850	2,900	1,770	1,700
Urban runoff and discharges	2,500	2,100	1,430 (700-2,800)	1,080 (500-2,500)
Losses from non-tanker shipping	750	200	340 (160-6,400)	320 (200-6,000)
Atmospheric deposition	600	600	300 (50-500)	300 (50-500)
Total	6,110	4,670	3,270	3,200
Percentage of totals				
Natural seeps	10	13	9	6
Extraction of petroleum	1	1	2	2
Transportation of petroleum	26	24	35	39
Consumption of petroleum	63	62	54	53

[a]Spills from pipelines were not specifically broken out, but appear to be included under coastal facility spills.

SOURCE: Compiled from GESAMP, 1993.

populations, while undoubtedly of interest, would overly complicate an already daunting task.) Based on these discussions, the NRC formally committed to undertake the study in the spring of 1998, and the Committee on Oil in the Sea was formed that summer (Appendix A; Box 1-2).

SOURCES, LOADS, FATES, AND EFFECTS

A comprehensive examination of the input, fates, and effects of petroleum hydrocarbons on the marine environment is a major undertaking. As is discussed in the subsequent chapters, the release of petroleum to the marine environment can take place in a wide variety of ways, and the size and impact of releases varies dramatically as each release involves a unique combination of physical, chemical, and biological parameters. An estimate of the total load of petroleum entering the marine environment worldwide, in and of itself, is not particularly meaningful, given the huge volume of water that comprises the global ocean. Petroleum entering the marine environment through spills or chronic releases, such as urban runoff, is eventually broken down or removed from the environment by natural processes or is diluted to levels well below even conservative concentrations of concern. However, from the time the material enters the environment until it is removed or sufficiently diluted, it does pose some threat to the environment. The magnitude of that threat varies dramatically depending of the size, composition, location, and timing of the release, the interactions of the introduced petroleum with various processes that affect the material after its introduction, and the sensitivity of the organisms exposed.

TABLE 1-3 Estimated Inputs from Shipping and Related Activities

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

SOURCE: GESAMP, 1993.

Regional or worldwide estimates of petroleum entering the environment are, therefore, useful only as a first order approximation of need for concern. Sources of frequent, large releases have been recognized as an area where greater effort to reduce petroleum pollution should be concentrated, despite the fact that not every spill of equal size leads to the same environmental impact. In addition, by attempting to repeat the development of estimates of petroleum pollution, a metric of performance for prevention efforts becomes available. This study, as did the 1975 and 1985 NRC reports, attempts to develop a sense of what the major sources of petroleum entering the marine environment are, and whether

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BOX 1-2
Statement of Task

The Committee on Oil in the Sea will attempt to identify, categorize, and quantify, to the extent possible, all sources of hydrocarbon input to the marine environment with an emphasis on North American waters. The committee will examine worldwide data in an effort to place numbers derived for North American waters into a global context. The committee will also assess knowledge, both quantitative and qualitative, about the fate and effects of fossil fuel hydrocarbons input to the marine environment.

Specifically the committee will—

- identify natural and anthropogenic sources of hydrocarbons entering the marine environment;
- identify and evaluate, to the extent possible, sources of quantitative information regarding the volume of hydrocarbon input to the marine environment worldwide from all sources;
- develop a methodology for evaluating the accuracy of estimates for hydrocarbon inputs from various sources;
- develop and summarize quantitative estimates of hydrocarbon inputs to the marine environment with an emphasis on North American waters;
- develop and summarize quantitative estimates of hydrocarbon inputs to the marine environment worldwide or for specific non-North American regions (as data and time permit);
- assess and discuss the physical and chemical characteristics and behavior of these hydrocarbons;
- assess and discuss the transport and fate of various hydrocarbon mixtures in the marine environment;
- assess and discuss the effects of these mixtures on marine organisms from subcellular to ecosystem level;
- evaluate, to the degree possible, the relative risk posed to the marine environment by each fossil fuel hydrocarbon mixture or type of input, given its source, abundance, and behavior, and the range of organisms or ecosystems affected.

these sources or the volume they introduce, have changed through time. To accomplish this goal, the committee considered the approaches used in earlier efforts and rapidly decided to develop new techniques based on more complete data or expanded knowledge. The values reported in the study, unless specifically attributed to other work, are therefore original estimates using the techniques discussed in the appendixes. In addition, considerable effort has gone toward making general conclusions about what kind of information is available, or needs to be made available, to move beyond the estimates themselves to a discussion of their significance of the release of petroleum in terms of impact to the environment. The fundamental nature of the problem has not changed significantly since 1985, but some progress has been made, especially in terms of our understanding of the pattern of petroleum release in North American waters and in the understanding of how petroleum can impact the environment. However, extrapolating from general estimates of volumes released to specific magnitude of effect at a given location is still largely beyond the ability of the science.

This report is an effort to strike a balance between providing a cogent analysis of the problem in a format accessible by a nontechnical reader and providing the technical underpinning for review and argument by a diverse, technically sophisticated audience. The remainder of the report is organized as follows. Chapter 2 provides an overview of the problem; presents the input estimates on a coarse, but understandable scale; and discusses recommendations for addressing the problem and expanding understanding. Some readers will necessarily want greater detail; thus, Chapter 3 discusses the input of petroleum to the sea in greater depth, Chapter 4 discusses the fate and transport of petroleum released to the environment in more detail, and Chapter 5 explores and synthesizes much of what has been learned about the effects of such releases on the environment since the early 1980s. Finally, the appendixes contain as much of the primary information used to derive the input estimates as practical. Appendixes C though J discuss the data, assumptions, and calculations used to develop the input estimates for readers who desire the greatest possible insight into their derivation.

PHOTO 3 Lightering oil from a supertanker at the Louisiana Offshore Oil Port in the Gulf of Mexico south of New Orleans. Tankers have historically been seen as a major source of oil pollution. Recent changes in tanker design (e.g., introduction of partitioned tanks and double hulls) and in oil handling procedures (e.g., offshore lightering) have significantly reduced the size and frequency of spills (Photo courtesy of Nancy Rabalias.)

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2

Understanding The Risk

HIGHLIGHTS

This chapter includes discussions of:

- The nature and composition of crude oil and petroleum products derived from it,
- The chemical, physical, and biological processes that affect how petroleum released into the marine environment behaves,
- Discussions of the principal sources of petroleum in the marine environment,
- Estimates of the mass of petroleum released to the marine environment each year from these sources,
- The potential environmental consequences of these petroleum releases, and
- A summary of the major findings and recommendations of the study.

Oil is a general term that describes a wide variety of natural substances of plant, animal, or mineral origin, as well as a range of synthetic compounds. Crude oil is a naturally occurring oil generated by geological and geochemical processes. A variety of petroleum products are then derived from this natural resource. Because their compositions vary, each type of crude oil or petroleum product has unique characteristics or properties. These properties influence how petroleum will behave when it is released and determine its effects on biota and habitats.

Crude oil and derived petroleum products (collectively referred to here as petroleum) are made up of dozens of major hydrocarbon compounds and thousands of minor ones. Hydrocarbons occur naturally in great abundance and in a variety of forms. Although petroleum is overwhelmingly composed of hydrocarbon compounds, not all hydrocarbon compounds come from petroleum. Thus, it is appropriate to limit discussion here to that subset of compounds typically associated with the term petroleum hydrocarbon. For the purposes of this study, hydrocarbon compounds containing less than five carbon atoms (e.g., methane, ethane, and other gases) were not considered because they are abundant and widespread and because their behavior differs so greatly from liquid petroleum. Furthermore, non-petroleum oils (e.g., vegetable oils, animal fats) were not included, because spills of these materials, although not trivial, present unique fate and effect problems. Addressing these spills in an adequate manner was determined to be beyond the resources of the present study.

Crude oil, the naturally occurring liquid form of petroleum, is an important part of the current energy mix of fossil fuels. As this fossil fuel is extracted, refined, transported, distributed, or consumed, spills and other releases occur. In addition, natural processes can result in seepage of crude oil from geologic formations below the seafloor to the overlying water column (see Chapter 3 for greater detail about natural and anthropogenic inputs). Understanding the nature and distribution of sources and their inputs, as well as the behavior of petroleum in the environment, is key for understanding the potential effect on the marine environment (see Chapters 4 and 5 for more detail about fate and effects).

THE COMPOSITION OF PETROLEUM

Petroleum is composed principally of hydrocarbons (compounds containing only hydrogen and carbon); thus, the terms petroleum and hydrocarbons are often used interchangeably. In fact, the elements hydrogen and carbon together (occurring as hydrocarbons or related compounds) constitute about 97 percent of most petroleum, while the

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minor elements nitrogen, sulfur, and oxygen make up the remaining 3 percent (NRC, 1985). Crude oil sometimes contains mineral salts, as well as trace metals such as nickel, vanadium, and chromium. In general, the hydrocarbon compounds found in crude oil are characterized by their structure (see Speight, 1991 for greater discussion of the classification of petroleum related compounds). These compounds include the saturates, olefins, aromatics, and polar compounds. Understanding these different compounds and their structures is important for understanding the fate and effect of releases of crude oil or products derived from it.

The saturate group of compounds in various crude oils consists primarily of alkanes, which are composed of hydrogen and carbon with the maximum number of hydrogen atoms around each carbon (Speight, 1991). Thus, the term "saturate" is used because the carbons are saturated with hydrogen. The saturate group also includes cycloalkanes, which are compounds made up of the same carbon and hydrogen constituents, but with the carbon atoms bonded to each other in rings. Higher-molecular-weight saturate compounds are often referred to as "waxes."

Olefins, or unsaturated compounds, are those that contain fewer hydrogen atoms than the maximum possible. Olefins have at least one carbon-to-carbon double bond, which displaces two hydrogen atoms. Significant amounts of olefins are found only in refined products (NRC, 1985; Speight, 1991).

Aromatic compounds include at least one benzene ring. Benzene rings are very stable, and therefore persistent in the environment, and can have toxic effects on organisms. The more volatile monoaromatic (single-ring) compounds found in crude oil are often referred to as BTEX, or benzene, toluene, ethylbenzene, and xylene (NRC, 1985; Speight, 1991).

Aromatic hydrocarbons may account for about 1 to 20 percent of the total hydrocarbons in crude oil. Benzene and alkyl benzenes with one or two methyl or ethyl groups (toluene, xylenes, ethylbenzene), the BTEX compounds, may be present at a concentration of several percent in light crude oil, but more typically are present at concentrations of 1,000 to 10,000 mg/kg (Speight, 1991). Usually, toluene is the most abundant of the BTEX compounds, followed by benzene or one of the three xylene isomers. More highly alkylated benzenes usually are present at low concentrations in crude oils.

Polycyclic aromatic (multiple-ring) hydrocarbons (PAH, also called polynuclear aromatic hydrocarbons, PNA) consist of at least two benzene rings. A typical crude oil may contain 0.2 percent to more than 7 percent total PAH.

Some related aromatic compounds (not technically hydrocarbons because they may contain within their structure many elements such as sulfur, nitrogen, and oxygen) are detected with the same analytical techniques and often occur with true polycyclic aromatic hydrocarbons. Thus, these compounds are often grouped with, and discussed as, PAH. PAH includes those compounds that have the most serious environmental effects of the compounds in crude oil. PAH in the environment are derived largely from combustion of oil and coal, but are also produced by the burning of wood, forest fires, and a variety of other combustion sources.

The abundance of aromatic hydrocarbons in petroleum usually decreases with increasing molecular weight. In most cases, one-ring (benzene) through three-ring (phenanthrene) aromatic hydrocarbons and related heterocyclic aromatic hydrocarbons, such as dibenzothiophene, account for at least 90 percent of the aromatic hydrocarbons that can be resolved in crude petroleum by conventional analytical methods (Neff, 1990). Four- through six-ring PAH (pyrene/fluoranthene through coronene), some of which are known mammalian carcinogens, usually are present at low or trace concentrations in crude oils (Kerr et al., 1999). The PAH in petroleum often contain one or more methyl, ethyl, or occasionally higher alkyl substituents on one or more aromatic carbons. As a general rule, these alkylated PAH are more abundant than the parent compounds in petroleum (Sporsol et al., 1983).

Of the hydrocarbon compounds common in petroleum, PAH appear to pose the greatest toxicity to the environment (see Chapter 5 for greater discussion). Most of the PAH compounds in petroleum are not as toxic as those produced by certain combustion processes, but most groups are significant components of runoff from paved surfaces.

Polar compounds are those that have a significant molecular charge as a result of bonding with elements such as sulfur, nitrogen, or oxygen. The polarity of the molecule results in behavior that differs from that of unpolarized compounds under some circumstances. In the petroleum industry, the smallest polar compounds are known as resins. The larger polar compounds are called asphaltenes and often make up the greatest percentage of the asphalt commonly used for road construction. Asphaltenes often are very large molecules, and if abundant in a specific volume of oil, they have a significant effect on oil behavior.

PROPERTIES OF CRUDE OIL OR PETROLEUM PRODUCTS

The properties of liquid petroleum, including crude oil or refined products, that are most important in understanding the behavior and fate of spills or other releases are viscosity, density, and solubility (see Chapter 4 for greater detail).

Viscosity is the resistance to flow in a liquid. The lower the viscosity, the more readily the liquid flows. The viscosity of oil or petroleum products is determined largely by the proportion of lighter and heavier fractions that it contains. The greater the percentage of light components such as saturates and the lesser the amount of asphaltenes, the lower is the viscosity. Highly viscous oils tend to weather more slowly because they do not spread into thin slicks. Instead, they form tarballs, which can be transported long distances and accumulate in thick deposits on shorelines that can persist for decades.

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Density is the mass of a given volume of oil or petroleum product and is typically expressed in grams per cubic centimeter.[1] It is the property used by the petroleum industry to define light or heavy crude oils. Density is also important because it indicates whether a particular oil will float or sink in water. The density of pure water is 1.0 g/cm^3 (at 15°C) and the density of most oils ranges from 0.7 to 0.99 g/cm^3 (at 15°C), thus most oils will float on water. Since the density of seawater is 1.03 g/cm^3 (at 15°C), thus even heavier oils will usually float on it. Density is often used as a surrogate for predicting the relative rate of natural weathering when crude oil or other petroleum products are released to the environment. Light oils contain petroleum hydrocarbons that are readily lost via evaporation and microbial degradation. Heavy oils contain a greater percentage of the higher-molecular-weight petroleum hydrocarbons that are more resistant to weathering.

Solubility in water is the measure of the amount of an oil or petroleum product that will dissolve in the water column on a molecular basis. Because the amount of dissolved oil is always small, this is not as significant a loss mechanism as evaporation. In fact, the solubility of oil in water is generally less than 100 parts per million (ppm). However, solubility is an important process because the water-soluble fractions of the oil are sometimes toxic to aquatic life. Thus, although solubilization represents a minor loss process, the concentration of toxic compounds dissolved in water from oil may be sufficient to have impacts on marine organisms.

BEHAVIOR IN THE ENVIRONMENT

Oil or petroleum products spilled on water undergo a series of changes in physical and chemical properties that, in combination, are termed "weathering." Weathering processes occur at very different rates but begin immediately after oil is released into the environment. Weathering rates are not consistent and are usually highest immediately after the release. Both weathering processes and the rates at which they occur depend more on the type of oil than on environmental conditions. Most weathering processes are highly temperature dependent, however, and will often slow to insignificant rates as the temperature approaches zero. Table 2-1 is a summary of the processes that affect the fate of petroleum hydrocarbons from seven major input categories. Each input is ranked using a scale of high, medium, and low that indicates the relative importance of each process. The table is intended only to convey variability and is based on many assumptions. Nevertheless, it does provide a general idea of the relative importance of these processes. Clearly one of the biggest problems in developing such a table is that the importance of a particular process will depend on the details of the spill event or release. Table 2-1 attempts to account for this to a limited extent in the case of accidental spills by including subcategories for various oil types (see Chapter 4). This table emphasizes the role various environmental processes can play in spills of widely varying types. This in turn underscores how just one facet of the complex set of variables may vary from spill to spill, making each spill a unique event. Thus, the chemical and physical character of crude oils or refined products greatly influence how these compounds behave in the environment as well as the degree and duration of the environmental effects of their release.

Relating Size of Release to Impact on Organisms

This report attempts to compile and estimate total release (or loadings) of petroleum hydrocarbons to the marine environment from a variety of sources. These loading rates, in units of mass per unit time, are useful to compare the relative importance of various types of loadings and to explore the spatial distribution of loadings. Obviously, sources of petroleum that release significant amounts (whether through spills or chronic discharges) represent areas where policymakers, scientists, and engineers may want to focus greater attention. Attributing specific environmental responses to loadings calculated at worldwide or regional scales, however, is currently not possible.

As discussed earlier, petroleum is a complex group of mixtures, and each group may contain widely varying relative amounts of hundreds (or more) compounds. Although many of the compounds are apparently benign, many other, such as some types of PAH, are known to cause toxic effects in some marine organisms. To further complicate this picture, marine organisms (even in the same taxa) vary greatly in their sensitivity to the same compound. Predicting the environmental response to a specific release of a known quantity of a refined petroleum product (which contains far fewer compounds than crude oil) requires much site-specific information about the nature of the receiving water body. Thus, the estimated loadings reported later in this chapter or in Chapter 3, are best used as a guide for future policymaking. In addition to identifying potential sources of concern, these estimates may have some value as performance metrics. Specifically, in those cases where reasonable comparisons can be made to estimates developed in earlier studies, they have value as a measure of the effectiveness of already implemented policies designed to reduce petroleum pollution.

Much of what is known about the impacts of petroleum hydrocarbons comes from studies of catastrophic oil spills and chronic seeps. These two aspects of petroleum pollution (loading and impact) are distinct, and it is not possible to

[1]The oil and gas industry, especially in the United States, often uses specific gravity instead of density. Specific gravity is used by the American Petroleum Institute (API) to classify various "weights" of oil. The density of a crude or refined product is thus measured as API gravity (ºAPI), which equals (141.5/specific gravity)—131.5.

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TABLE 2-1 Processes That Move Petroleum Hydrocarbons Away from Point of Origin

Input Type	Persistence	Evaporation	Emulsification	Dissolution	Oxidation	Horizontal Transport or Movement	Vertical Transport or Movement	Sedimentation	Shoreline Stranding	Tarballs
Seeps	years	H	M	M	M	H	M	M	H	H
Spills										
Gasoline	days	H	NR	M	L	L	L	NR	NR	NR
Light Distillates	days	M	L / L	H	L	M	H	L	L	NR
Crudes	months	M	M	M	M	M	M	M	H	M
Heavy Distillates	years	L	M	L	L	H	L	H	H	H
Produced water	days	M	NR	M	M	L	L	L	L	NR
Vessel operational	months	M	L	M	L	M	L	L	L	M
Two-stroke engines	days	H	NR	M	L	L	L	NR	NR	NR
Atmospheric	days	H	NR	M	M	H	NR / NR	NR	NR	NR
Land based	U	M	L	L	L	M	M	M	NR	U

NOTE: H = high; L = low; M = moderate; NR = not relevant; U = unknown

directly assess environmental damage from petroleum hydrocarbon mass loading rates. As discussed in Chapters 4 and 5 to a very large degree, loading rates reflect the intensity and location of societal use of petroleum, whereas effects tend to reflect the amount of toxic hydrocarbon compounds reaching a marine organism and the differing susceptibility of various organisms, populations, and ecosystems to the effects of these hydrocarbons. **The reader is therefore strongly cautioned against inferring impacts from the mass loading rates.** For instance, one might be tempted to calculate the "*Exxon Valdez*-equivalence" by comparing the quantity of petroleum released from a specific source to that released during the *Exxon Valdez* spill and then concluding that the impact of the petroleum release will be a corresponding multiple of the *Exxon Valdez* impact. This is a flawed analysis. Ecotoxicological responses are driven by the dose of petroleum hydrocarbons available to an organism, not the amount of petroleum released into the environment. Because of the complex environmental processes acting on the released petroleum, dose is rarely directly proportional to the amount released. In addition, one must consider the type of petroleum released and the susceptibility of the target organisms. Complex geochemical and pharmacokinetic models are required to translate petroleum release rates into environmental exposures. Even once these factors are accounted for, it is often difficult to reach consensus on the magnitude and duration of environmental effects (Box 2-1).

The amount of petroleum made available to an organism through various environmental processes (whether for ingestion or absorption) is referred to as being biologically available, or simply "bioavailable." Just as combustion during smoking makes nicotine in tobacco bioavailable to the smoker, physical, chemical, and even biological processes determine how bioavailable toxic compounds in oil and other petroleum products will be to marine organisms. It is understandable, therefore, that the release of equal amounts of the same substance at different times or locations may have dramatically different environmental impacts.

Broadly speaking, the term "bioavailability" can therefore be used to describe the net result of physical, chemical, and biological processes that moderate the transport of hydrocarbon compounds from their release points to the target organisms. As the spill moves from the release point to the marine organism, these processes alter the chemical composition of the petroleum mixture, which in turn likely alters the toxicity by selectively enriching or depleting the toxic components (Bartha and Atlas, 1987). Physical weathering processes (Table 2-1) may encapsulate some or all of the petroleum in forms that are less available to organisms (e.g., tarballs). Various physiological and behavior processes moderate the movement of petroleum from the surrounding environment into marine organisms. Individual petroleum components pass into organisms at different rates, depending on their physical and chemical properties. Organisms respond to hydrocarbons in their surroundings and moderate or accentuate exposure. Incidental ingestion of oil by preening birds enhances exposure, while short-term cessation of filter feeding by bivalves in response to hydrocarbons in the water limits exposure. Once the hydrocarbons are in the organisms, there is a wide variation in the types and magnitudes of physiological responses. Many organisms readily metabolize and excrete hydrocarbons, although these pathways may create more toxic intermediates. In short, the processes of bioavailability, including petroleum fate and transport in the coastal ocean and disposition within marine organisms, are the most complex and least understood aspects of oil in the sea. Although there is a reasonable understanding of the amount of petroleum hydrocarbons released to the coastal ocean, and one can estimate the impact of spilled petroleum under previously studied conditions, generalizing these findings to predict hydrocarbon impacts from all sources on North American coastal waters is currently not possible.

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BOX 2-1

Lessons from *Exxon Valdez*: Science in a Litigious Environment

In addition to being the largest oil spill in U.S. waters, the *Exxon Valdez* Oil Spill (EVOS) has been a seminal event in the development of U.S. environmental policy. Efforts to ascertain the extent of the injury and the rate of recovery from the spill have been particularly divisive and opposing positions have been hotly debated.

The relevant federal regulation (43 CFR 11.14) provides definitions of both injury and recovery, but does not specify how these are to be objectively measured. Thus, both the responsible party (Exxon) and the resource trustees (EVOS Trustee Council) developed different perspectives on how to define both injury and recovery, these differences reflecting very real differences in each group's political, social, and financial objectives and responsibilities.

These different perspectives and objectives led to differing technical and scientific approaches or methods for quantifying both the extent of the initial injury and the rate of recovery. These different approaches then led to different results and conflicting, and often incompatible, conclusions from two sets of studies. At the core of many disagreements centering on uncertainty in cause and effect were the questions of burden of proof and the application of the precautionary principle. In general, Exxon demanded a high level of proof to accept an injury, whereas the Trustees used a weight-of-evidence approach that accepted higher levels of uncertainty.

Such situations are not uncommon in the world of science. Science is often divisive. In fact, the scientific method uses trial-and-error hypothesis testing and peer criticism to develop understanding in the form of a consensus opinion. Thus, scientific understanding is often best developed under a dynamic tension between consensus building and division. Litigation, however, offers a drastically different and somewhat incompatible set of rules. The purpose of litigation (from the latin *litigāre,* to dispute, quarrel, sue) is to resolve differences by determining which party has the stronger of two legal arguments. As in many instances where scientific or technical evidence forms the central tenant of either party's argument, the dynamic tension between consensus building and division shifts perceptibly and inextricably toward division. Finding common ground in a litigious environment is not a priority, in fact it may even be considered to be antithetic to the purpose of litigation. Thus, while scientific and technical questions that arise within the litigious environment surrounding an event like EVOS may have broad implications for fundamental scientific understanding of the way systems respond to perturbations, the totality of the scientific effort expended during litigation cannot reasonably be expected to lead to a consensus opinion.

This was recognized early on in the post-EVOS world, and a growing desire to inject new approaches or philosophies to facilitate cooperative approaches for developing natural resource damage assessments (NRDAs) began to emerge. Eventually, using authority granted under the Oil Pollution Act of 1990 (commonly referred to as OPA 90), NOAA instituted a new set of NRDA regulations that codified steps to develop cooperative assessment plans involving both the responsible party and the resource trustees. Under these regulations, responsible parties must be given the opportunity to participate in the damage assessment and, when appropriate, jointly conduct a coordinated and open damage assessment. The invitation to participate must be in writing and as early as practical, but no later than the completion of the preliminary assessment phase of the incident. There should be a formal agreement on how the cooperation is to be structured. The process should be open and all results available to the public.

There are many benefits of cooperative assessments: cost savings because only one set of studies is being conducted; less potential for litigation because both sides are working with the same data and are more likely to reach common ground; and restoration can be accomplished more quickly because efforts can be shifted to designing restoration projects rather than preparing for litigation.

Inherent in the cooperative process is trust. Each group has to trust the other to make a good faith effort to make the process succeed. Otherwise, there is the fear that cooperation will be abused: one side uses the knowledge gained in the process to build a better legal defense; studies are intentionally designed to provide data that are too weak for use in litigation; one side only pretends to be working cooperatively, or only agrees to cooperate on data collection and initial analysis, then the case changes to an uncooperative process for final negotiations and litigation, leaving the other side with a weaker case.

Ongoing and future efforts to define the injury and recovery of the ecosystem in and around Prince William Sound due to EVOS will continue to raise important scientific questions and will contribute greatly to scientific understanding of the effect of releases of petroleum at a variety of scales. However, the development of a consensus opinion regarding the answers to these same questions most likely lies outside research efforts currently embroiled in the EVOS litigation.

Understanding the Impacts of Spills and Other Releases

Oil in the sea, whether from spills or chronic sources, is perceived as a major environmental problem. Occasional major oil spills receive considerable public attention because of the obvious attendant environmental damage, oil-coated shorelines, and dead or moribund wildlife, including, in particular, oiled seabirds and marine mammals (Box 2-2). These acute effects may be of short duration, or they may have long-term population- or community-level impacts depending on the circumstances of the spill and the numbers and types of organisms affected. Oil in the sea also occurs when small amounts are released over long periods of time, resulting in chronic exposure of organisms to oil and its component chemical compounds. Sources of chronic exposures include point sources, such as natural seeps, a leaking pipeline,

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A

B

C

D

PHOTO 4 Each year since 1990, scientists studying shoreline recovery following the *Exxon Valdez* spill in Prince William Sound have taken photos of a prominent boulder, know commonly referred to as Mearns Rock. The photo series, available at http://response.restoration.noaa.gov/photos/mearns/mearns.html, demonstrates the complex changes that can take place year to year in the nature and abundance of marine organisms. ***(A)*** **1991** The entire boulder is covered with *Fucus sp*., a gold-brown algae. Notice the darker species of seaweed forming an apron around the base of the boulder. The beach area surrounding the boulder (the "beach face") is also completely covered with other seaweed species. In the water behind the boulder, healthy eelgrass (*Zostera marina*) bed is visible. The boulder's condition appears to be improving, shown by the heavier covering of seaweed. ***(B)*** **1993** *Fucus* now covers about 20 percent of the boulder's surface. Large, older plants are gone apparently replaced by young plants. Mussels are growing on the front face of the boulder (black regions). ***(C)*** **1995** About half of the mussels have disappeared, leaving smaller dark regions on the right side of the boulder. *Fucus* is making a comeback on the left side and top surface of the boulder. Also visible is an apparent resurgence of algal growth on the beach face. The disappearance of the mussels may be the result of predation (perhaps by sea otters) or natural mortality. Regardless of whatever caused the boulder's plant life to die back in 1993-94, the boulder now seems to be supporting new plant and animal life. ***(D)*** **1997** The boulder is once again covered (about 80 percent) with the seaweed *Fucus*. There are several age groups of *Fucus* on the boulder. Young *Fucus* is growing over the top section of the boulder and adult *Fucus* is growing around the mid-portion. The beach face is again rich with seaweed. No mussels are visible and the areas occupied by the barnacles have shrunk. Starfish and sea otters may have been preying on the mussels, and a predatory snail, *Nucella*, has likely been eating the barnacles.

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E

F

PHOTO 4 (continued) ***(E)*** **2000** Mature *Fucus* now covers about 10 percent of the boulder's surface. In addition, there is a heavy cover of a grayish, slimy seaweed (this could be any of three or four seaweed species that can look like this). The white areas on the beach face look to be large barnacle sets. Eelgrass is barely visible in the water. As in the 1993 photo, the mature *Fucus* plants are again dying back. However, at this time, there is no sign of a third new crop of young *Fucus*. ***(F)*** **2001** This year, the boulder has a 20-30 percent cover of *Fucus*. Older (brownish) plants are visible on the left section of the boulder and younger (greenish-brown) plants on the right. A whitish "bald" patch on the upper left is actually a patch of barnacles. Another bare-looking patch on the lower right corner contains barnacles (white) and small mussels (dark spots). A bright green algae, possibly "sea lettuce" *(Ulva)* droops down along the lower third of the rock face. Algae and barnacles also cover most of the cobble on the beach face. (Photo by Alan Mearns, courtesy of NOAA Office of Response and Restoration.)

BOX 2-2

Environmental Sensitivity Index Mapping

In 1979, as the oil from the Ixtoc II well blowout approached the U.S. coast, the Scientific Support Team from the Hazardous Materials Response Branch of the National Oceanic and Atmospheric Administration (NOAA) was advising the U.S. Coast Guard on protection priorities. The concept of ranking shorelines according to their oil spill sensitivity had recently been developed (Michel et al., 1978), and it was first applied in the days prior to oil landfall in south Texas. In 1980, the first Environmental Sensitivity Index (ESI) maps were produced for south Florida; by 1990, hardcopy ESI maps were available for most of the U.S. coastline.

Since 1990, updated maps have been produced using Geographical Information System (GIS) technology, with both hard copy and digital products available. ESI maps and databases are comprised of three general types of information (Fig. 2-1; Halls et al., 1997):

Shoreline Classification. The shoreline habitats are ranked according to a scale relating to sensitivity, natural persistence of oil, and ease of cleanup. A scale of 1 to 10 is used, with 1 being least sensitive and 10 the most sensitive. The classification system has been standardized nationwide, for estuaries, rivers, and lakes. The ranking scheme is based on extensive, empirical observations at oil spills, and it has become the basis for many spill response tools and strategies, such as protection prioritization, selection of response options, and determination of cleanup endpoints.

Biological Resources. The maps display the spatial and temporal distributions of oil-sensitive animals, habitats, and rare plants that are used by oil-sensitive species or are themselves sensitive to oil spills. There are seven major biological groups (marine mammals, terrestrial mammals, birds, fish, invertebrates, reptiles and amphibians, and habitats and plants), which are further divided into groups of species with similar taxonomy, morphology, life history, and/or behavior relative to oil spill vulnerability and sensitivity. The maps show the locations of the highest concentrations, the most sensitive life-history stages or activities, and the most vulnerable and sensitive species. The maps link to data tables that include species name, legal status of each species (state and/or federal threatened or endangered listing), concentration at that specific location, seasonal presence and/or abundance by month, and special life-history time periods (e.g., for birds, nesting, laying, hatching, and fledging dates).

Human-Use Resources. The maps show four specific areas that have increased sensitivity and value because of their use: high-use recreational and shoreline access areas; management areas (e.g., marine sanctuaries and refuges); resource extraction locations (e.g., water intakes, subsistence areas); and archaeological, historical, and cultural resource locations.

Sensitivity maps are used to identify protection priorities in vessel and facility response plans, and they are used in area contingency plans as part of the Sensitive Areas Annex. ESI maps use a standard set of colors and symbology so responders from any region can use the maps readily. The concept of sensitivity mapping has been adopted internationally as a key component of oil spill contingency planning (Baker et al., 1995). Sensitivity atlases have been produced for such diverse areas as Australia, Mauritius, South Africa, the Gaza Strip, the North Sea, most of Canada, and the Sakhalin Islands.

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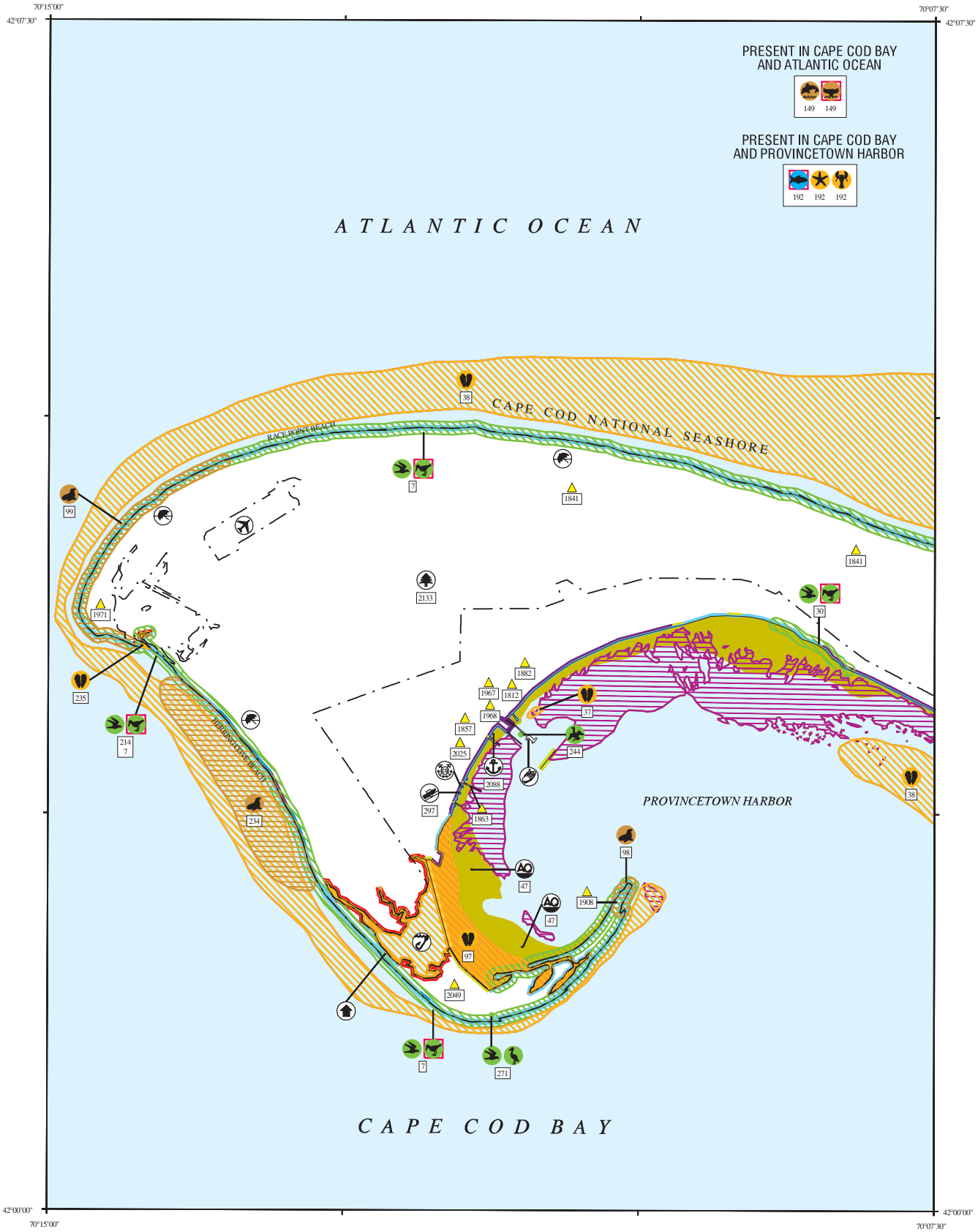

FIGURE 2-1 Environmental Sensitivity Index Map, with legend, for Provincetown Harbor, Cape Cod, Massachusetts (courtesy Research Planning, Inc.).

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MASSACHUSETTS

SHORELINE HABITAT RANKINGS

- 1A) EXPOSED ROCKY SHORES
- 1B) EXPOSED, SOLID MAN-MADE STRUCTURES
- 2A) EXPOSED WAVE-CUT PLATFORMS IN BEDROCK
- 3A) FINE- TO MEDIUM-GRAINED SAND BEACHES
- 3B) SCARPS AND STEEP SLOPES IN SAND
- 4) COARSE-GRAINED SAND BEACHES
- 5) MIXED SAND AND GRAVEL BEACHES
- 6A) GRAVEL BEACHES
- 6B) RIPRAP
- 7) EXPOSED TIDAL FLATS
- 8A) SHELTERED ROCKY SHORES
- 8B) SHELTERED, SOLID MAN-MADE STRUCTURES
- 8C) SHELTERED RIPRAP
- 9A) SHELTERED TIDAL FLATS
- 9B) VEGETATED LOW BANKS
- 10A) SALT- AND BRACKISH-WATER MARSHES
- 10B) FRESHWATER MARSHES
- 10C) SWAMPS

HUMAN-USE FEATURES

- ACCESS
- AIRPORT
- AQUACULTURE
- AREA OF CRITICAL ENVIRONMENTAL CONCERN (ACEC)
- BOAT RAMP
- COAST GUARD
- COMMERCIAL FISHING
- FERRY
- LOCK OR DAM
- MARINA / ANCHORAGE
- MARINE SANCTUARY / RESERVE
- NATIONAL PARK
- RECREATIONAL BEACH
- RECREATIONAL FISHING
- STATE PARK / FOREST
- WASHOVER SITE
- WATER INTAKE
- WILDLIFE REFUGE / MGT AREA
- HISTORICAL SITE
- 123 HUMAN-USE NUMBER
- STATE BOUNDARY
- MANAGEMENT AREA
- BRIDGE

SENSITIVE BIOLOGICAL RESOURCES

BIRD
- DIVING BIRD
- GULL / TERN
- PELAGIC BIRD
- RAPTOR
- SHOREBIRD
- WADING BIRD
- WATERFOWL
- NESTING SITE

FISH
- ANADROMOUS STREAM
- BEGINNING OF RUN

INVERTEBRATE
- BIVALVE
- INSECT

MARINE MAMMAL
- DOLPHIN
- PINNIPED
- WHALE

REPTILE
- TURTLE

SUBMERSED HABITAT
- EELGRASS

ELMR (FISH & INVERTEBRATE)
- FISH
- CRUSTACEAN
- ECHINODERM

- THREATENED / ENDANGERED
- 123 RAR NUMBER

SALINITY INFORMATION (ALL ESTUARIES)

DECREASING SALINITY PERIOD	LOW SALINITY PERIOD	INCREASING SALINITY PERIOD	HIGH SALINITY PERIOD
October - February	March - May	June	July - September

HIGH SALINITY
HIGHER
LOWER

LOW SALINITY
HIGHER
LOWER

FISH AND INVERTEBRATES RELATIVE ABUNDANCE

1 No Information
2 Rare
3 Common
4 Abundant
5 Highly Abundant

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production discharges, or a land-based facility. In these cases, there may be a strong gradient from high to low oil concentration as a function of distance from the source. In other cases, such as land-based runoff and atmospheric inputs, the origin of the oil is a non-point source, and environmental concentration gradients of oil compounds may be weak. Chronic exposures may also result from the incorporation of oil into sediments in which weathering of oil is slow and from which nearly fresh oil may be released to the water column over extended periods. In recent years, it is the long-term effects of acute and chronic oil contamination that have received increasing attention (Boesch et al., 1987)

Petroleum Hydrocarbon Pollution and Its Possible Effects

Petroleum hydrocarbon inputs into North American and worldwide marine waters were computed, based on various databases, for several major categories. Three activities—extraction, transportation, and consumption—are the main sources of anthropogenic petroleum hydrocarbon pollution in the sea. Each of these activities poses some risk of oil release, and as greater amounts of petroleum hydrocarbons are imported into North American waters, the risk increases. The categories are listed in Table 2-2. Details of the methods used, discussion of databases, and computation and distribution of sources are discussed in Appendixes C, D, E, F, G, H, and I. Table 2-2 and Figures 2-2A and 2-2B summarize the sources and inputs for North American and worldwide waters (see Chapter 3 for greater details). Table 2-3 summarizes conclusions about the intercomparability of the data, methods, and assumptions used develop these estimates with those reported by the NRC in 1985 and what significance if any, can be attached to changes in those estimates.

The acute toxicity of petroleum hydrocarbons to marine organisms is dependent on the persistence and bioavailability of specific hydrocarbons. The ability of organisms to accumulate and metabolize various hydrocarbons, the fate of metabolized products, the interference of specific hydrocarbons (or metabolites) with normal metabolic processes that may alter an organism's chances for survival and repro-

TABLE 2-2 Average, Annual Releases (1990-1999) of Petroleum by Source (in thousands of tonnes)

	North America[a]				Worldwide		
	Best Est.	Regions[b]	Min.	Max.	Best Est.	Min.	Max.
Natural Seeps	**160**	**160**	**80**	**240**	**600**	**200**	**2000**
Extraction of Petroleum	**3.0**	**3.0**	**2.3**	**4.3**	**38**	**20**	**62**
Platforms	0.16	0.15	0.15	0.18	0.86	0.29	1.4
Atmospheric deposition	0.12	0.12	0.07	0.45	1.3	0.38	2.6
Produced waters	2.7	2.7	2.1	3.7	36	19	58
Transportation of Petroleum	**9.1**	**7.4**	**7.4**	**11**	**150**	**120**	**260**
Pipeline spills	1.9	1.7	1.7	2.1	12	6.1	37
Tank vessel spills	5.3	4.0	4.0	6.4	100	93	130
Operational discharges (cargo washings)	na[c]	na	na	na	36	18	72
Coastal facility spills	1.9	1.7	1.7	2.2	4.9	2.4	15
Atmospheric deposition	0.01	0.01	trace[d]	0.02	0.4	0.2	1
Consumption of Petroleum	**84**	**83**	**19**	**2000**	**480**	**130**	**6000**
Land-based (river and runoff)	54	54	2.6	1900	140	6.8	5000
Recreational marine vessel	5.6	5.6	2.2	9	nd[e]	nd	nd
Spills (non-tank vessels)	1.2	0.91	1.1	1.4	7.1	6.5	8.8
Operational discharges (vessels ≥100 GT)	0.10	0.10	0.03	0.30	270	90	810
Operational discharges (vessels<100 GT)	0.12	0.12	0.03	0.30	nd[f]	nd	nd
Atmospheric deposition	21	21	9.1	81	52	23	200
Jettisoned aircraft fuel	1.5	1.5	1.0	4.4	7.5	5.0	22
Total	**260**	**250**	**110**	**2300**	**1300**	**470**	**8300**

[a]Numbers are reported to no more than two significant figures.

[b]"Regions" refers to 17 zones or regions of North American waters for which estimates were prepared. These are discussed later in this chapter.

[c]Cargo washing is not allowed in U.S. waters, but is not restricted in international waters. Thus, it was assumed that this practice does not occur frequently in U.S. waters (see Chapter 3 and Appendix E).

[d]Estimated loads of less than 10 tonnes per year reported as "trace."

[e]Worldwide populations of recreational vessels were not available (see Chapter 3 and Appendix F).

[f]Insufficient data were available to develop estimates for this class of vessels (see Chapter 3 and Appendix E).

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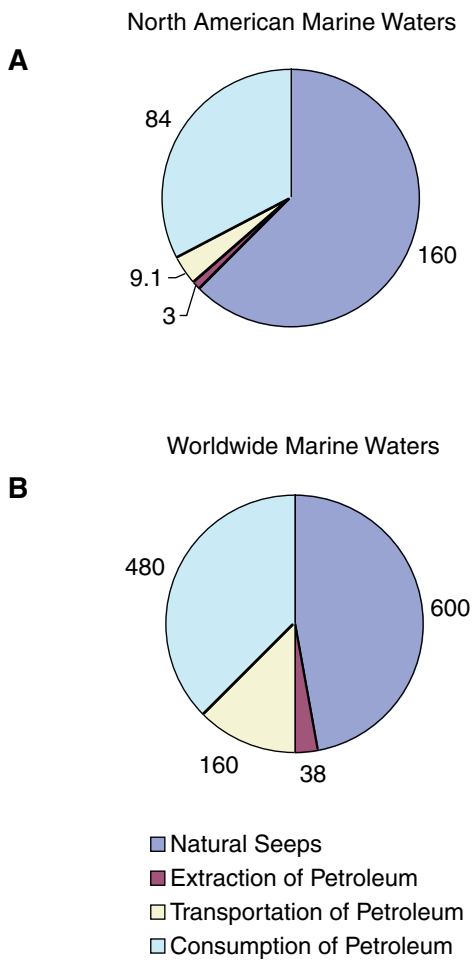

FIGURE 2-2 Relative contribution of average, annual releases (1990-1999) of petroleum hydrocarbons (in kilotonnes) from natural seeps and activities associated with the extraction, transportation, and consumption of crude oil or refined products to the marine environment.

duction in the environment, and the narcotic effects of hydrocarbons on nerve transmission are major biological factors in determining the ecologic impact of any release. Weathering processes may alter oil composition and thus its toxicity (Burns et al., 2000; Neff et al., 2000). With weathering, there is a subsequent loss of monoaromatic compounds, and the polycyclic aromatic hydrocarbons become more important contributors to the toxicity of weathered oils. Other factors that may contribute to alterations in toxicity include photodegradation and photoactivation (Mallakin et al., 1999; Boese et al., 1999).

Data gathered from several spills that occurred in the 1970s and 1980s demonstrated that the higher molecular weight aromatic compounds, such as the alkylated phenanthrenes and alkylated dibenzothiophenes, are among the most persistent compounds in both animal tissues and sediments (Capuzzo, 1987). Impairment of feeding mechanisms, growth rates, development rates, energetics, reproductive output, recruitment rates and increased susceptibility to disease and other histopathological disorders are some examples of the types of sublethal effects that may occur with exposure to petroleum hydrocarbons (Capuzzo, 1987). Early developmental stages can be especially vulnerable to hydrocarbon exposure, and recruitment failure in chronically contaminated habitats may be related to direct toxic effects of hydrocarbon-contaminated sediments (Krebs and Burns, 1977; Cabioch et al., 1980, Sanders et al., 1980; Elmgren et al., 1983).

Marine birds and mammals may be especially vulnerable to oil spills if their habitats or prey become contaminated. In addition to acute effects such as high mortality, chronic, low-level exposures to hydrocarbons may affect survival and reproductive performance of seabirds and some marine mammals. Sublethal effects of oil on seabirds include reduced reproductive success and physiological impairment, including increased vulnerability to stress (reviewed in Hunt, 1987; Fry and Addiego, 1987, 1988; Briggs et al., 1996). In contrast, in marine mammals, sublethal exposure to petroleum hydrocarbons has been shown to cause minimal damage to pinnipeds and cetaceans (e.g., Geraci, 1990; St. Aubin, 1990), although sea otters appear to be more sensitive (Geraci and Williams, 1990; Monson et al., 2000). Oil can also indirectly affect the survival or reproductive success of marine birds and mammals by affecting the distribution, abundance, or availability of prey.

Oil inputs from consumption activities vary widely in composition, persistence, loading rates by area and season, and effects. The single largest inputs of both petroleum hydrocarbons and PAH from this general source are land-based sources, which are composed of petroleum hydrocarbons that have already undergone considerable chemical and biological weathering during overland and riverine transport by the time they enter coastal waters. Further weathering rates will be slow. The hydrocarbons are mostly sorbed onto suspended sediments; thus their bioavailability is highly variable, depending on the feeding behavior of different organisms, sediment deposition patterns and rates, organic carbon content of the sediments, and the partitioning behavior of individual PAH. In contrast, although the input from the operation of recreational marine vessels in coastal waters is large, the bulk of the fuel is gasoline, which volatilizes from the surface water at rates that last on the order of several minutes to hours at 15°C. The temporal and spatial discharge patterns are different from other sources, with most recreational boating being concentrated in the summer months and in coastal waters.

Chronic contamination by petroleum hydrocarbons from sources other than oil spills may be found in many coastal urban areas as a result of non-point source petroleum spillage, the burning of fossil fuels, and municipal wastewater discharges. The persistence of some compounds such as PAH in sediments, especially in urban areas with multiple

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TABLE 2-3 Validity and Significance of Comparisons Between Estimates from NRC (1985) and Current Report

This Report	1985 Report	Comparability	Significance of change in estimate
Natural Seeps	Marine Seeps	Changes in methods, data, and assumptions significant, but gross comparison still valid.	Natural seeps are a significant source in both reports.
	Sediment erosion	Differences in approach for calculated land-based loads prevent direct comparison.	Both reports point out that at worldwide or continental scales, the load from eroded source rocks is overwhelmed by natural seeps or anthropogenic loads from land-based sources. Thus, these sources may be of local significance in areas where seeps or anthropogenic loads are essentially absent.
Extraction of Petroleum	Offshore production	Changes in groupings of subcategories make direct comparison with 1985 study impossible.	
Platforms	Platforms and pipelines	Both studies used national databases as the foundation for the resulting estimate. However, the 1985 report combined spills from pipelines with platforms. Thus, combining the estimates for these two sources in the current study should allow valid comparison at two significant figures.	Reduction in worldwide estimate from 40,000 tonnes per year to 13,000 tonnes per year is significant and is believed to reflect changes in industry practice, especially in areas where stricter regulations have been implemented.
Produced waters	Operational (produced water) discharges	Basic approach was similar but the most significant difference was in how the volume of produced water was determined. In 1985, produced water was determined as a fraction of oil production. The current study used reported data on produced water volume for North America and the North Sea, and extrapolations to worldwide production. Also, oil content was based on actual reported measurements in North America and the North Sea.	The increase from roughly 10,000 tonnes per year to 36,000 tonnes per year is significant, mostly reflecting an increase in the amount of produced water discharged as oil production fields mature, but also related to increased offshore oil production.
Atmospheric deposition		Not accounted for in 1985 study.	Small number calculated in the current study suggests the input is significant only in terms of its impact on local air quality.
Transportation of Petroleum	Transportation	Changes in groupings of subcategories make direct comparison with 1985 study impossible. Combining estimates for relevant categories (tanker operations, dry docking, marine terminals, bilge & fuel oil, tanker accidents, non-tanker accidents) in current study allows for valid comparison at two significant figures.	The decrease from 1.5 million tonnes to 420,000 tonnes is significant and reflects the substantial steps taken to reduce the incidence of transportation related spills and operational discharges worldwide.
Pipeline spills		Included with platforms in 1985 study.	
Spills (tank vessels)	Tanker accidents	Both studies used international databases as the foundation for the resulting estimate. Thus, the results should be grossly comparable at two significant figures.	The decrease from 700,000 tonnes per year to 100,000 tonnes is significant and reflects the substantial steps taken to reduce the incidence of transportation-related spills worldwide.
Operational discharges (cargo oil)	Tanker operations	Differing quality of data and changes in methodology make comparisons of little value.	
Coastal facility spills	Dry-docking	Both studies used international databases as the foundation for the resulting estimate. However, nature and type of facilities included makes comparison of limited value.	
	Marine terminals	Grouped with Dry Docking and Refineries in current study.	
	Refineries	Grouped with Dry Docking and Marine Terminals in current study.	
Atmospheric deposition (tanker VOC)		Not accounted for in 1985 study.	Small number calculated in the current study suggests the input is significant only in terms of its impact on local air quality.

continues

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TABLE 2-3 Continued

This Report	1985 Report	Comparability	Significance of change in estimate
Consumption of Petroleum		Changes in groupings of subcategories make direct comparison with 1985 study impossible.	
Land-based (river and runoff)	Municipal & industrial wastes	Significant differences in data quality, assumptions, and methodology make comparison meaningless.	The large numbers suggested by both studies, although not directly comparable, suggest that land-based sources of petroleum pollution to coastal environments is a significant environmental concern at a variety of scales.
	Municipal wastes	Grouped with all land-based sources in current report.	
	Non-refinging industrial wastes	Grouped with all land-based sources in current report.	
	Urban runoff	Grouped with all land-based sources in current report.	
	River runoff	Grouped with all land-based sources in current report.	
Recreational marine vessels		Not accounted for in 1985 study.	Large number calculated during current study suggests this may be an important source of petroleum pollution, especially given the environmental sensitivity of the coastal areas where these vessels most commonly operate.
Spills (commercial vessels ≥100 GT)	Nontanker accidents	Both studies used national databases as the foundation for the resulting estimate. Thus, the results should be comparable at two significant figures.	The decrease from 20,000 tonnes per year to 7,100 tonnes is significant and reflects the substantial steps taken to reduce the incidence of transportation-related spills worldwide.
Operational discharges (vessels ≥100GT)	Bilge and Fuel oils	Differences in data, assumptions, and methodology make comparison of little value.	
Operational discharges (vessels <100GT)		1985 study did not differentiate based on vessel size.	
Atmospheric deposition	Atmosphere	Differences data, assumptions, and methodology make comparison of limited value.	Large numbers calculated in both studies suggest this may be a significant input of petroleum (especially PAH) to the marine environment
Jettisoned aircraft fuel		Not accounted for in 1985 study.	Large number (7,500 tonnes worldwide) suggests that this source may generate significant loading at local scales.
	Ocean dumping	Not accounted for in current study.	Ocean disposal of wastewater treatment/sewage sludge has been banned in the United States and elsewhere, but may be locally significant where practiced. However, given the large uncertainty already associated with estimates of land-based sources (2 orders of magnitude), calculating the additional loads to each region or worldwide from sludge disposal was deemed to be of limited value.

sources of petroleum inputs, is an example of chronic persistence and toxicity beyond the observations made following oil spills. Meador et al. (1995) reviewed the processes controlling the uptake and persistence of PAH in marine organisms, especially under chronic exposure conditions, highlighting differential mechanisms of tissue distribution and elimination. Transfer of contaminants to marine biota and the human consumer and toxicological effects on the ecosystem are dependent on the availability and persistence of these contaminants within benthic environments. The incidence of tumors and other histopathological disorders in bottom-dwelling fish and shellfish from contaminated coastal areas has been suggested as a possible link to chronic hydrocarbon exposure and uptake (Neff and Haensly, 1982; Berthou et al., 1987; also see Chapter 5).

To understand the toxic effects of petroleum hydrocarbon releases to the marine environment, one has to examine the loading of the more toxic components of the hydrocarbon mixture. Since PAH are thought to be responsible for many of the biological effects of petroleum, estimates of PAH

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TABLE 2-4 Estimated PAH Contribution to North American Waters and Assumptions of Oil Type Composition by Source

Source	Description of Composition by Oil Type	Estimated PAH Contribution (thousands of tonnes per year)
Natural Seeps	Crude oil	2.5
Petroleum Extraction		
Platforms	Crude oil, heavy distillates, light distillates, and gasoline	0.0016
Produced waters	Crude oil	0.052
Atmospheric deposition	See Chapter 3 and Appendix D	0.016
Subtotal		0.070
Petroleum Transportation		
Vessel spills	Crude oil, heavy distillates, light distillates, and gasoline	0.12
Pipelines	Crude oil, heavy distillates, light distillates, and gasoline	0.030
Coastal facilities	Crude oil, heavy distillates, light distillates, gasoline	0.0040
Atmospheric deposition	See Chapter 3 and Appendix E	0.016
Subtotal		0.17
Petroleum Consumption		
Land-based	See Chapter 3 and Appendix I	0.54
Aircraft dumping	Jet fuel	0.031
Recreational vessels	Lube oil	0.0015[a]
< 100 GT vessels	Light distillates	0.0040
> 100 GT vessels	Heavy distillates and light distillates	0.0084
Atmospheric deposition	See Chapter 3 and Appendix H	1.60
Subtotal		2.2
Total		4.9

[a]Pyrogenic PAH produced during incomplete combustion is not included in this value, which must therefore be considered as a minimum estimate.

loads from various petroleum sources were derived for the major sources of petroleum (Table 2-4). Although these numbers may have value as first-order indicators of where loads of PAH may be important, it is important to note that the toxic effect of specific PAH compounds differ from that of the entire class. Furthermore, sensitivity to various specific PAH compounds can vary dramatically among species, even among closely related taxonomic groups (see Chapter 5). As with other effects from spills, the timing and nature of introduction of PAH, as well as the environmental processes (see Chapter 4) operating at the time, can play a significant role in determining the ultimate toxicological effect these compounds may have.

Many of the source types, including natural seeps, platforms, pipelines, produced waters, vessel spills, vessel operations, aircraft dumping, recreational marine vessels, vessels of less than 100 GT, and coastal facilities, PAH loadings were estimated as a fraction of the total petroleum hydrocarbon loadings, based on measured PAH content of crude oils and refined petroleum products (see Appendix J). Because coastal waters are undersaturated with dissolved PAH relative to the overlying atmosphere, there is a significant net transfer of atmospheric PAH to the oceans. PAH loadings from land-based sources were estimated by assuming that the PAH load from each river is proportional to the estimated petroleum hydrocarbon loading (see Chapter 3 and Appendix E for details). This refinement of the 1985 report *Oil in the Sea* is a step toward a more rigorous risk assessment of petroleum releases to the coastal oceans.

A significant effort was made to develop estimates of inputs by zone, both along shore regions and two zones offshore (a coastal zone that extended out to 3 miles and an offshore zone from 3-200 miles). This effort, to further delineate the geographic distribution of these inputs, is the second significant difference between the current study and the 1985 *Oil in the Sea* report, led to the subdivision of North American waters into 17 zones (Figure 2-3). These values were totaled to develop the first approximation of total inputs to the North American and world-wide marine environment listed in Table 2-2 (values reported in the "Regions" column). This regional approach allows the spatial distribution of the inputs to be used as a basis for evaluating the potential risks of the oil inputs to marine resources in each region (Fig. 2-4). It is clear that the ecological effects of oil inputs is a function of many factors, including oil type, release rates, fate processes, and distribution of biological resources. It is difficult to articulate in general terms how each of the input categories may affect marine resources because of the wide range of pathways of exposure, species sensitivity, and potential effects. Regional data may be of benefit to

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regulators and resource managers, by helping to establish linkages between petroleum inputs and potential effects, leading to prioritized actions needed to reduce the most significant risks.

Natural Seeps

Natural seeps are the highest contributors of petroleum hydrocarbons to the marine environment (Figures 2-2A and 2-2B). Coastal seeps occur mainly in southeast Alaska where they are a minor source of petroleum introduced to the region during the reporting period (1990-1999).[2] Offshore seeps are only known to occur in the northern and southern Gulf of Mexico, where they represent 95 percent of the total oil inputs to the offshore region, and southern California, where they represent 98 percent of oil inputs to the offshore zone. Considering the size of the inputs into these regions, and that the releases are composed primarily of unweathered crude oil, one would expect seeps to have a significant impact to marine resources in these areas. Yet, studies have shown that benthic communities have acclimated and even evolved to utilize some of the hydrocarbons (Spies et al., 1980; Spies and Desmaris, 1983; Montagna et al., 1986, 1989). The uncertainty in these estimates is large, complicating attempts to understand the potential risks to marine ecosystems. It is also uncertain whether the rates of release from seeps will decrease as the reservoirs are depleted over the next coming decades.

Crude oil released as seeps constitutes the single largest source of PAH input to the sea; however, these seeps most often occur in specific oil-production areas, and release rates are relatively low and chronic. As the relatively unweathered crude oil enters the ocean from the seabed, the soluble compounds dissolve and the volatile compounds volatilize, but much of the oil rises to the surface, forming slicks. For most crude oils, about one-third is lost by evaporation-volatilization in the first 24 hours. Intermediate-weight compounds can degrade by photooxidation and microbial processes over periods of weeks, and the residues form tarballs. Where seeps occur close to shore, such as in the Santa Barbara Channel off the coast of southern California, tar forms persistent deposits on the shoreline. Seeps are a significant contributor to the coastal PAH budget, adding 2.5 thousand metric tonnes, or one half of the estimated annual PAH loading (Table 2-4). Unlike much of the coastal waters, waters in areas dominated by seeps are likely enriched in dissolved PAH, and net volatilization of PAH occurs.

Petroleum seeps occur in many parts of the ocean and have served as natural experiments for understanding the relationship between chemical persistence and biological response among organisms comprising the seep community, including adaptive responses that have occurred over generations of exposure. As petroleum enters the ocean from the seabed, it is relatively unweathered and provides an energy source to microbial populations (Bauer et al., 1988; Spies et al., 1980; Spies and Desmaris, 1983; Montagna et al, 1986, 1989). This enrichment of the benthic environment by microbial turnover of organic material alters the benthic community by depleting local oxygen concentrations in addition to altering the hydrocarbon concentrations for exposure.

The most detailed investigations of petroleum seepages have been carried out in the Santa Barbara Channel off the coast of southern California. In heavy seepage areas, the benthic community has low diversity of a few species or invertebrates and is dominated by mats of sulfur-oxidizing bacteria (*Beggiatoa*) and a few species of invertebrates (Spies et al., 1980; Montagana et al., 1987, 1989, 1995). Pore-water concentrations of aromatic hydrocarbons within a few centimeters of an active seep were about 1 ppm. Within several meters of the very active seeps and where a small amount of seepage is still found, a diverse benthic community exists, similar in composition to benthic communities of the inner continental shelf in southern California with a few differences in species abundance (Spies, 1987). Natural biogeochemical tracers (^{13}C, ^{14}C, ^{35}S) indicate that both the petroleum carbon, particularly the lighter fractions, and the sulfur from sulfide are incorporated into benthic meiofauna and macrofauna (Spies and DesMarais, 1983; Bauer et al., 1990). **Therefore, even though the input from seeps is very large, ecological impacts appear to be limited in area, suggesting that the slow rate of release allows biota to acclimate to PAH and other toxic compounds in the releases.**

Extraction of Petroleum

Historically, extraction of petroleum hydrocarbons has represented a significant source of spills and other releases of petroleum to the marine environment. The second largest marine spill event in the world was the IXTOC I blowout that released 476,000 tonnes of crude oil into the Gulf of Mexico in 1979. In the past decade, however, improved production technology and safety training of personnel have reduced significantly both blowouts and daily operational spills. Today, roughly 150 tonnes of petroleum hydrocarbons per year are discharged as accidental spills from platforms in North American waters (Table 2-2). Another source of petroleum hydrocarbon pollution in the extraction process is from produced waters. Presently, this is the largest source, approaching 2,700 tonnes per year into North American waters and 36,000 tonnes worldwide (Table 2-2). Although these amounts may seem high at first glance, these contributions represent less than 2 percent of the amount entering the marine environment from natural sources (Figures 2-5A and 5B).

[2]As discussed in Chapter 3 and Appendix I, erosion of organic rich source rocks can yield petroleum-bearing sediment in locally significant amounts. However, this material is largely bound within sediment particles, thus suggesting it is largely not biologically available.

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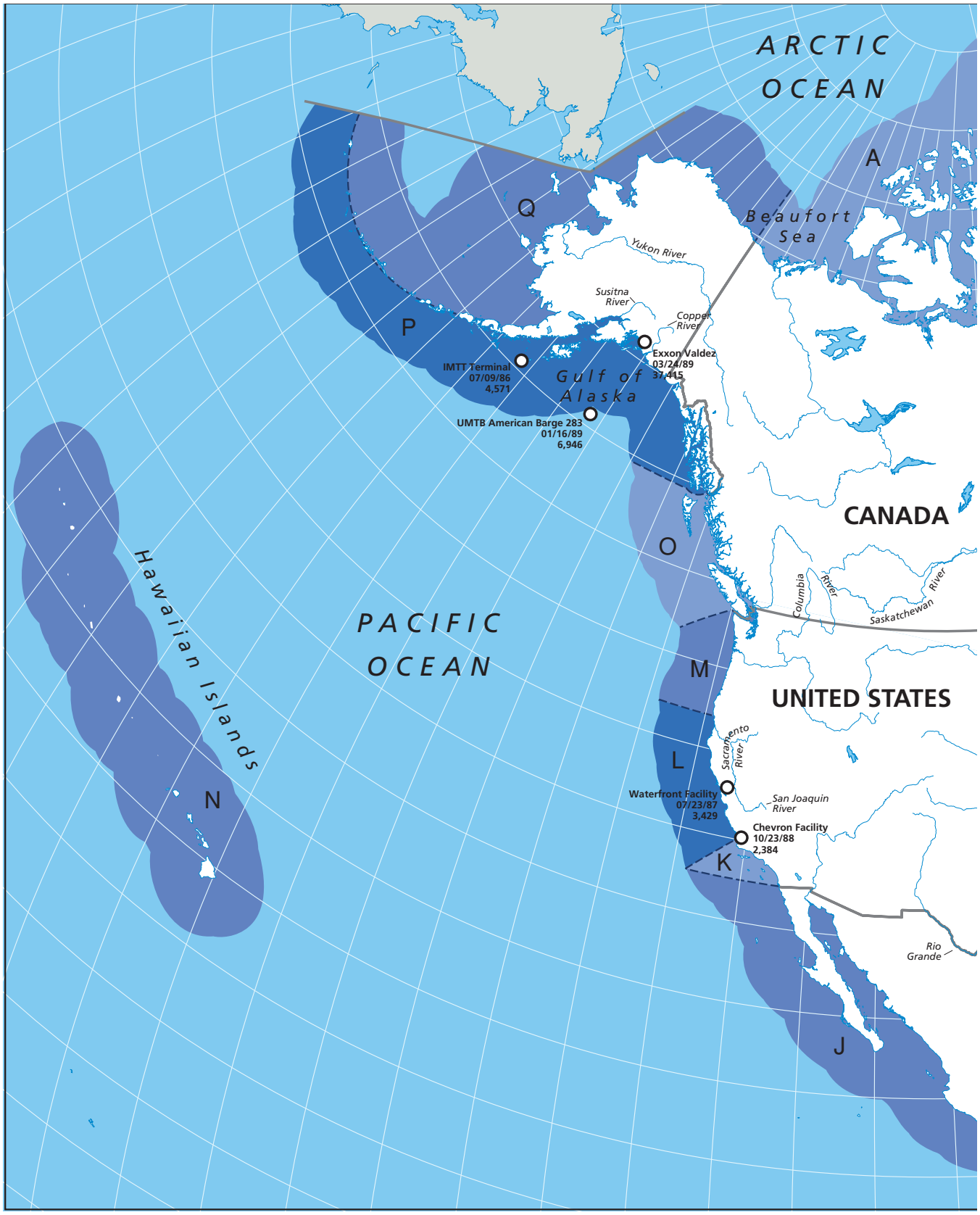

FIGURE 2-3 Distribution of 17 North American marine zones discussed in this report. (Additional information provided by U.S. Coast Guard and Minerals Management Service.) Solid black dots indicate spills included in the average, annual (1990-1999) estimates discussed in this report.

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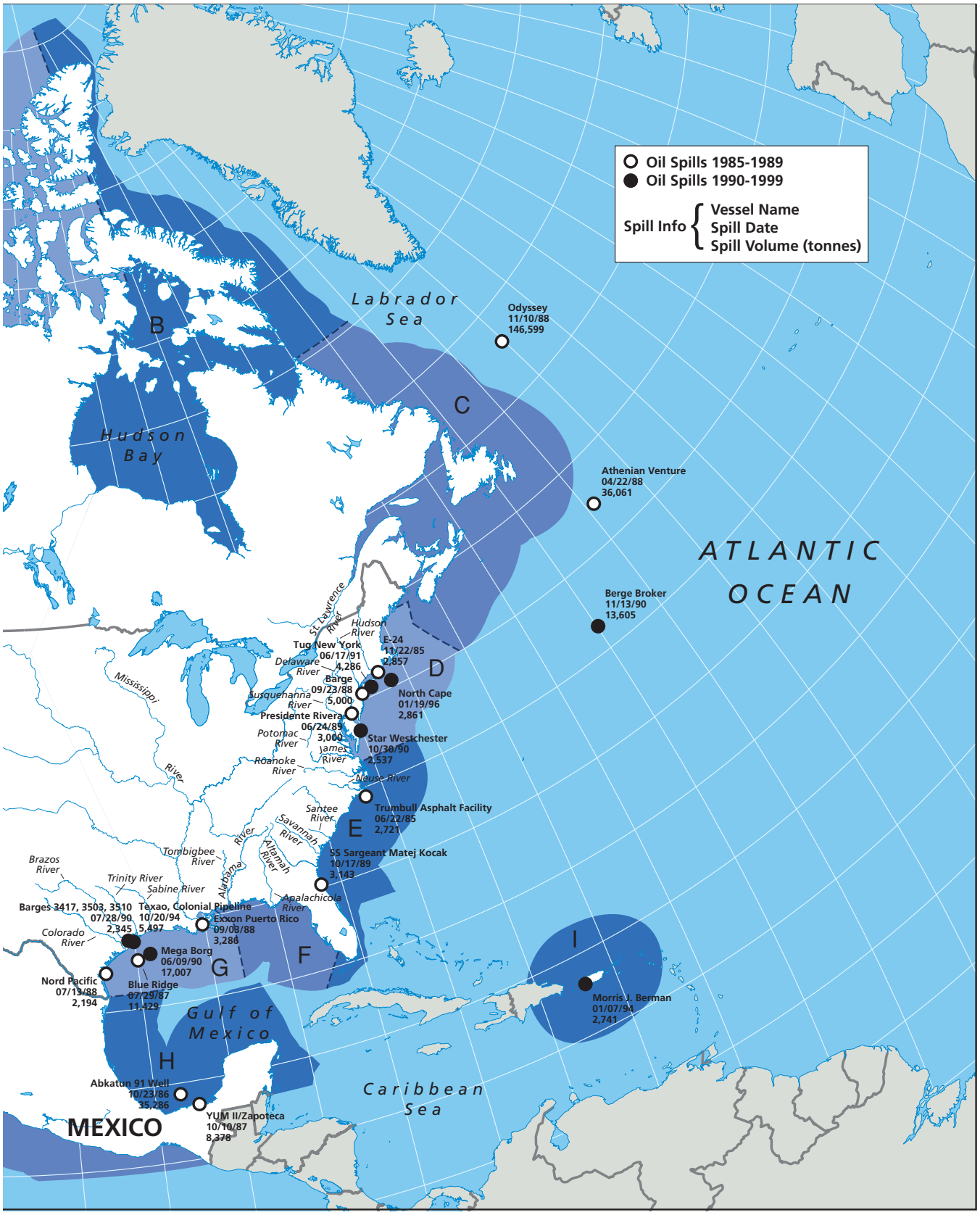

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FIGURE 2-4 Geographic variation in average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) to the North American marine environment.

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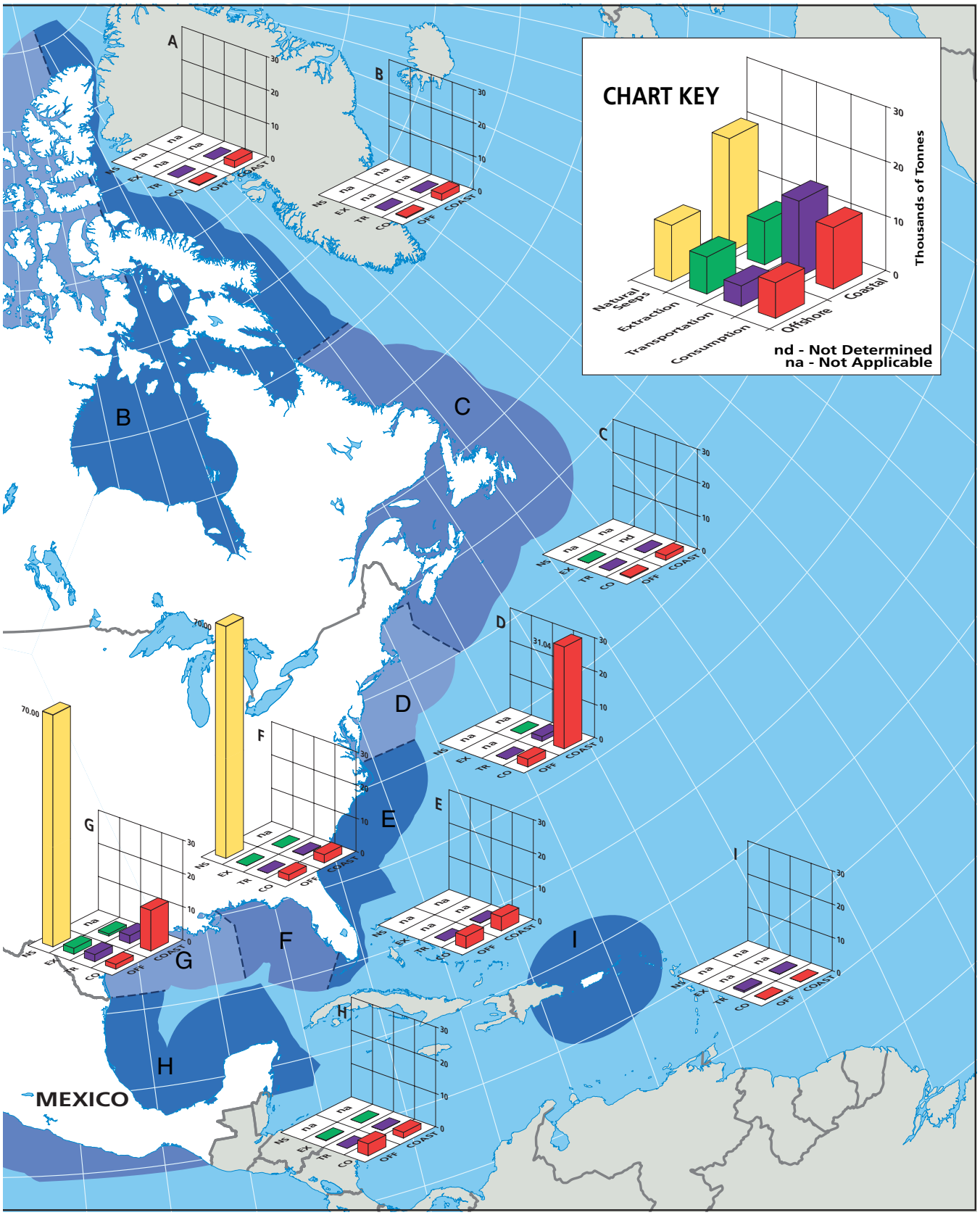

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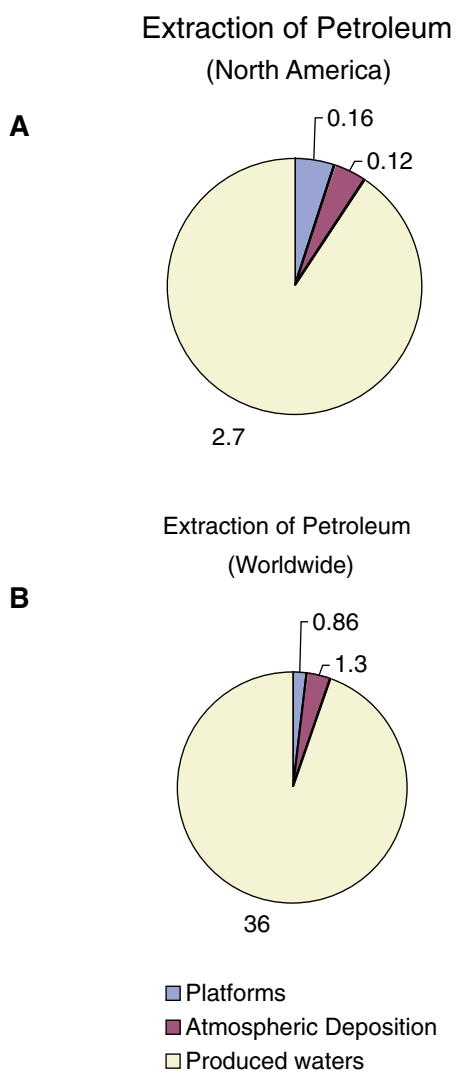

FIGURE 2-5 Relative average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) to North American (A) and worldwide (B) marine environment from sources associated with petroleum extraction.

Inputs from oil and gas extraction are restricted to the coastal and offshore oil and gas production areas, namely the Gulf of Mexico, Alaska, southern California, and Canadian Maritimes (Fig. 2-6). Over 90 percent of the inputs from extraction activities are from produced water discharges (Fig. 2-5), which release low but continuous amounts of dissolved components and dispersed crude oil (Utvik, 1999). Because dilution and weathering are important mechanisms for reducing the concentrations of toxic components in produced water, the elimination of coastal discharges in most North American waters has significantly reduced the overall potential effects of these inputs. Similar discharges continue, however, in production fields of developing countries.

Spills (of mostly crude oil) from platforms comprise 5 percent of the total inputs from extraction activities. The amount of oil released into the coastal zone for the Canadian Maritimes, eastern Gulf of Mexico, and southeast Alaska are remarkably similar, ranging from 2.2 to 2.5 tonnes per year. Oil input from platform spills into California coastal waters is very low, at 0.4 tonnes per year. The highest amount of oil from platform spills is for the northwestern Gulf of Mexico, with inputs into coastal waters reaching 81 tonnes per year and representing 92 percent of the total amount of oil spilled from platforms into North American coastal waters. Spills into state waters are about twice the input from spills in offshore waters. Spills from platforms are generally small, averaging 3.5 tonnes (1,000 gallons), yet small spills can have significant impacts under some circumstances.

Extraction activities do not appear to be an important source of PAH. Less than 2 percent of the 5,000 tonnes of PAH entering the marine environment comes from petroleum extraction (Table 2-4). Extraction activities release about 0.07 thousand tonnes of PAH to marine waters in North America, with 74 percent associated with produced water discharges. Most of the remaining PAH inputs resulting from extraction activities are from atmospheric deposition.

Inputs from extraction of petroleum are composed primarily of components of crude oil, although they also include minor spills of refined products from equipment and vessel operations associated with oil platforms (see Chapter 3). The single largest input from extraction activities is from produced waters that contain the dissolved compounds (mostly single-ring aromatic hydrocarbons) and dispersed oil that cannot be separated from the water extracted with the oil from reservoirs (see Table 2-2). The dissolved compounds are also relatively volatile, so a significant fraction of the oil from produced water is removed rapidly by volatilization and evaporation, particularly when released to open, well-mixed waters. The finely dispersed oil droplets stay suspended in the water column and undergo microbial degradation or are sorbed onto suspended sediments that are then deposited on the seabed (Boesch and Rabalais, 1989a). Elevated levels of contaminants in sediments typically extend up to 300 m from the discharge point. Produced water discharges increase with reservoir age; thus these inputs may increase over time unless more produced water is re-injected or better treatment technologies are developed.

Except for very rare blowouts, spills from platforms are generally small and make landfall only when spilled close to shore or inshore. Impacts would be greatest in coastal or inland areas where numerous small spills result in chronic exposure during the life of the field. Oil production in coastal waters only occurs in Louisiana, Texas, and Alaska, although most of it is in Louisiana.

The environmental effects that may result from oil and gas production in a field depend greatly on the characteristics of the receiving environment (Rabalais et al., 1991a, Rabalais et al., 1992). Measurable effects are most likely in

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shallow waters, areas of restricted flow and dispersion, water with a high concentration of suspended particulates, and fine-grained anaerobic sediments (Boesch and Rabalais, 1989 a,b; St. Pé, 1990). There are clear effects of produced water discharges on estuarine waters, sediments, and living resources in inshore production fields where the receiving environment is not conducive to the dispersion of the effluent plume. In the United States, studies of their effects (Boesch and Rabalais, 1989 a,b; St. Pé, 1990; Rabalais et al., 1991a) led to the prohibition of produced water discharges into coastal waters in the late 1990s. In shallow shelf waters, hydrocarbons from produced water accumulate in bottom sediments, and the diversity of benthic fauna may be reduced up to 300 m from the outfall (Rabalais et al., 1991a,b; also see Chapter 5; Table 5-7). Measurable effects occur around offshore platforms but, except for artificial reef effects (sedimentary changes or changes brought about by a cuttings pile), such effects are usually localized (Rabalais et al., 1993; Kennicutt et al., 1996a; Montagna and Harper, 1996). It is noted, however, that discharge of oil-based drill cuttings has never been permitted in the U.S. and was recently prohibited in the North Sea. Beyond some contamination of organisms by petroleum, there is little convincing evidence of significant effects from petroleum around offshore platforms. Where oil-based drill cuttings are discharged, there are more readily evident effects of sediment contamination and benthic impacts to much greater distances from the platforms (up to 1 to 2 km) (see Chapter 5). Although directed studies have identified some specific sublethal effects of long-term oil and gas development (Kennicutt et al., 1996a, b; Street and Montagna, 1996), the most significant unanswered questions remain those regarding the effects on ecosystems of long-term, chronic, low-level exposures resulting from discharges and spills caused by development activities. Unique features of deep-sea communities and the relative lack of understanding of these communities may make them more vulnerable to production activities. **As the reservoirs age, the volume of produced water discharges from existing production facilities will significantly increase. The ecological impact of increasing rates of produced water discharge in both nearshore and new deep-water habitats is not clear. It will be important to consider these increases in future monitoring programs.**

Another component of crude oil that is released during petroleum extraction consists of the VOC that occur as gases at ambient temperature and pressure, and thus escape to the atmosphere. Atmospheric deposition from extraction activities accounts for 4 percent of the total extraction-related inputs. Because VOC inputs are estimated using production volume, inputs are largest for the areas of highest oil and gas production. Inputs into coastal waters are about an order of magnitude lower than into offshore areas (see Table 2-2).

Only 0.2 percent of the VOC released to the atmosphere are estimated to be deposited into surface waters, when very conservative assumptions are used. This input is overwhelmed by hydrocarbon outgassing from the oceans. **Therefore, impacts from VOC deposited at relatively low, uniform rates over large areas of ocean are likely to be small. Still, the fate and potential effects of VOC inputs to marine ecosystems are poorly understood; thus, there are unanswered questions about the concentrations and duration of VOC in the microlayer, the bioavailability of such volatile compounds, and their toxicity.**

Transportation of Petroleum

The five major sources of petroleum hydrocarbon discharges into the marine waters by transportation activities include pipeline spills, tank vessel spills, operational discharges from cargo washings, coastal facilities spills, and gross atmospheric deposition of VOC releases from tankers (Table 2-2, Figures 2-7 and 2-8).

Pipelines

DeLuca and LeBlanc (1997) estimate that there are approximately 23,000 miles of pipelines that carry petroleum hydrocarbons in North America. Pipeline spills can occur as petroleum hydrocarbons are transported from the source to refineries and from refineries to the consumer (see Chapter 3 for greater details). The total input of petroleum hydrocarbons to the marine environment by spills from pipelines to North American waters is estimated to be 1,900 tonnes per year (Fig. 2-7).

The volume of crude oil spilled from pipelines in coastal areas is double that spilled in offshore areas, increasing the potential impacts because weathering and fate processes will not reduce the risks of exposure from such spills of crude oil (see Chapter 3). Accidental spills by pipelines are more common in coastal waters because production first occurred in the coastal regions and many of the pipelines are approaching 30–40 years old. It is highly probable that accidental spills from coastal pipelines will continue into the future as these pipelines age further unless steps are taken to ensure the integrity of this important system. **The efforts of the Office of Pipeline Safety, under the Pipeline Integrity Management Program, are timely and appropriate for reducing these risks.**

Tanker Spills

Because of numerous regulations and technology advances in vessel construction (i.e., double-hull tankers, new construction materials, and vessel design) spills from tank vessels have been reduced significantly during the past decade, even though the tanker fleet has increased by some 900 vessels to a total of 7,270 in 1999. Spills greater than 34 tonnes in size represent less than 1 percent of the spills by number but are responsible for more than 80 percent of the total spill volume (see Chapter 3 for greater details). In North American waters, vessel spills have been reduced consider-

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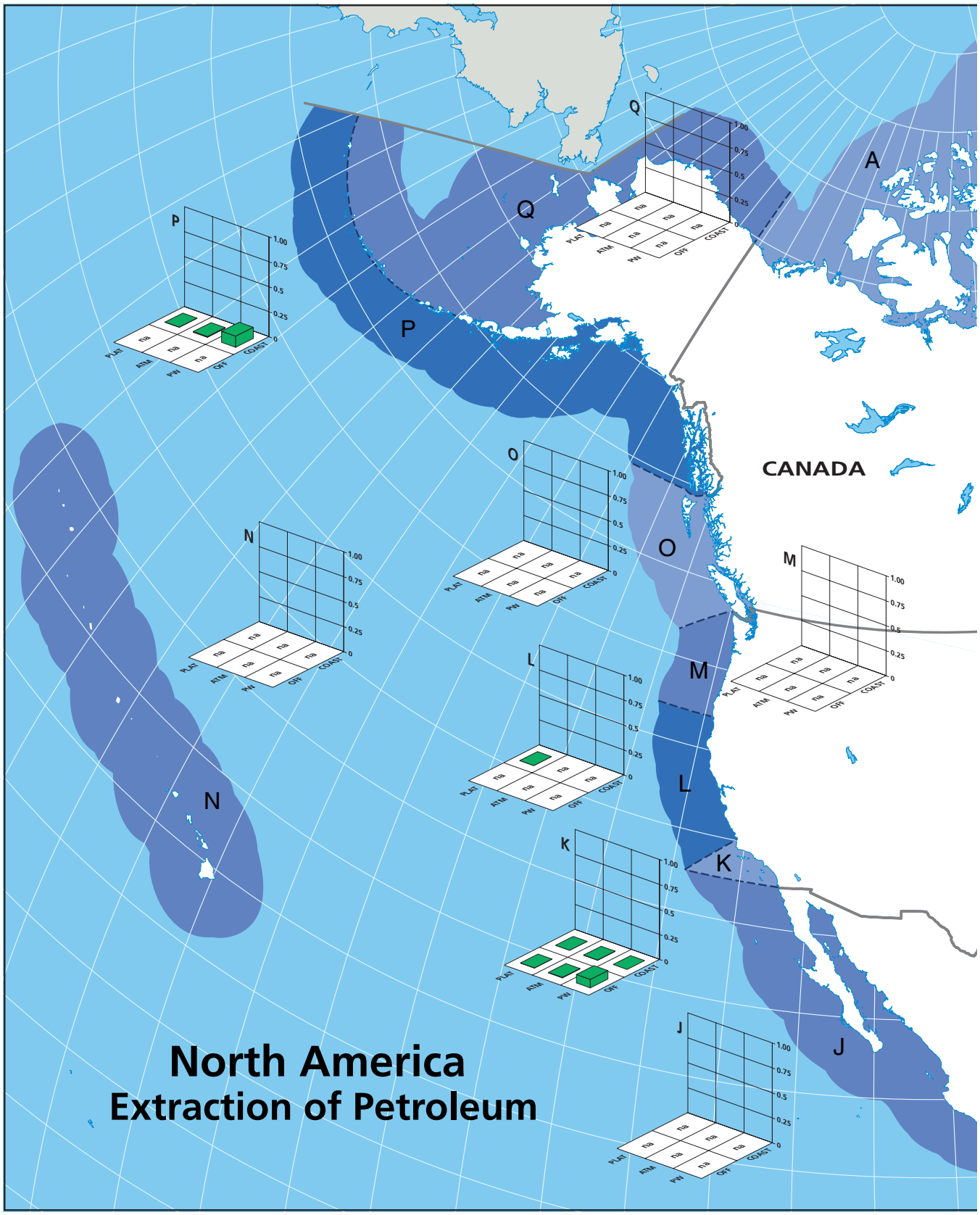

FIGURE 2-6 Geographic variation in average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) to the North American marine environment from sources associated with petroleum extraction.

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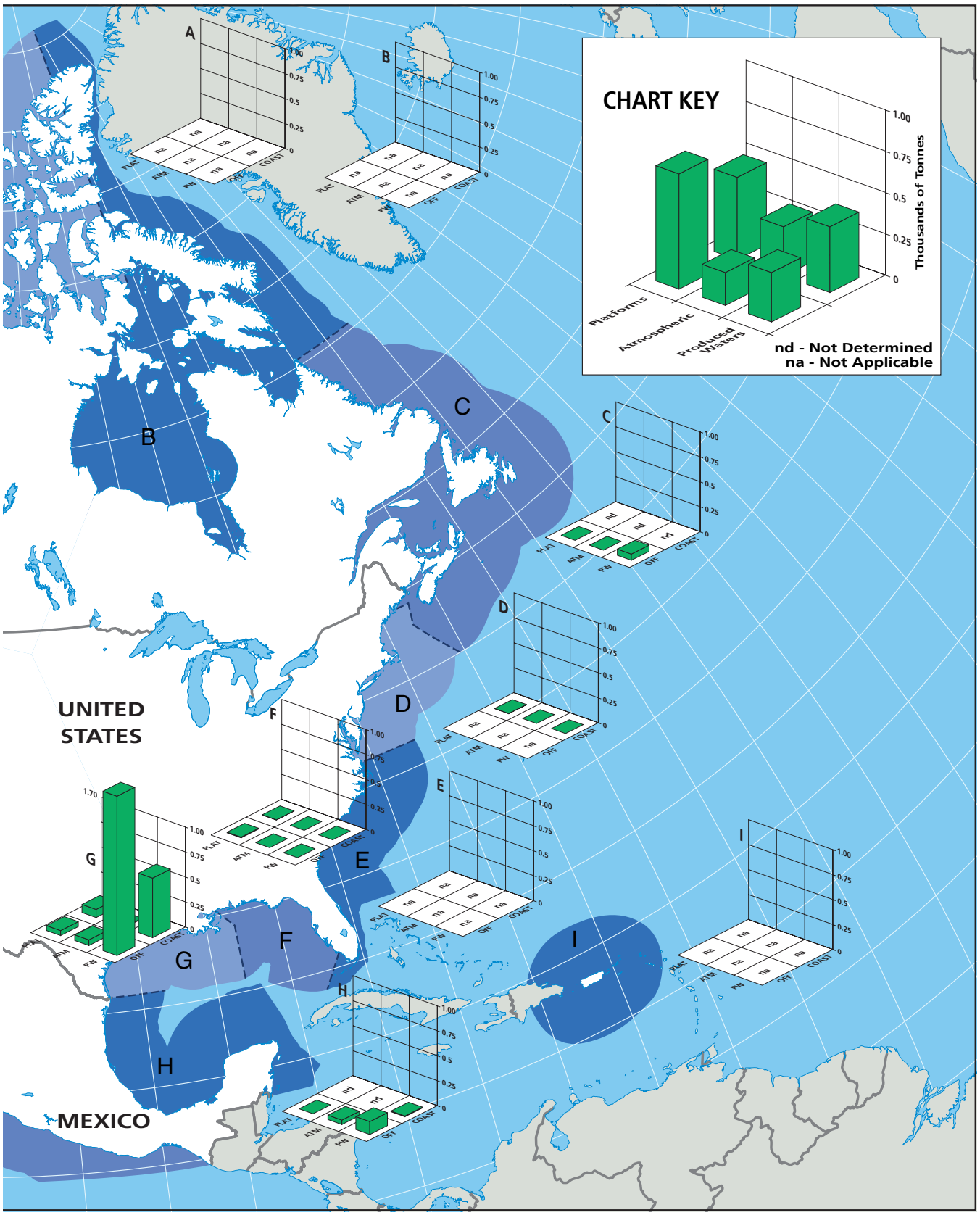

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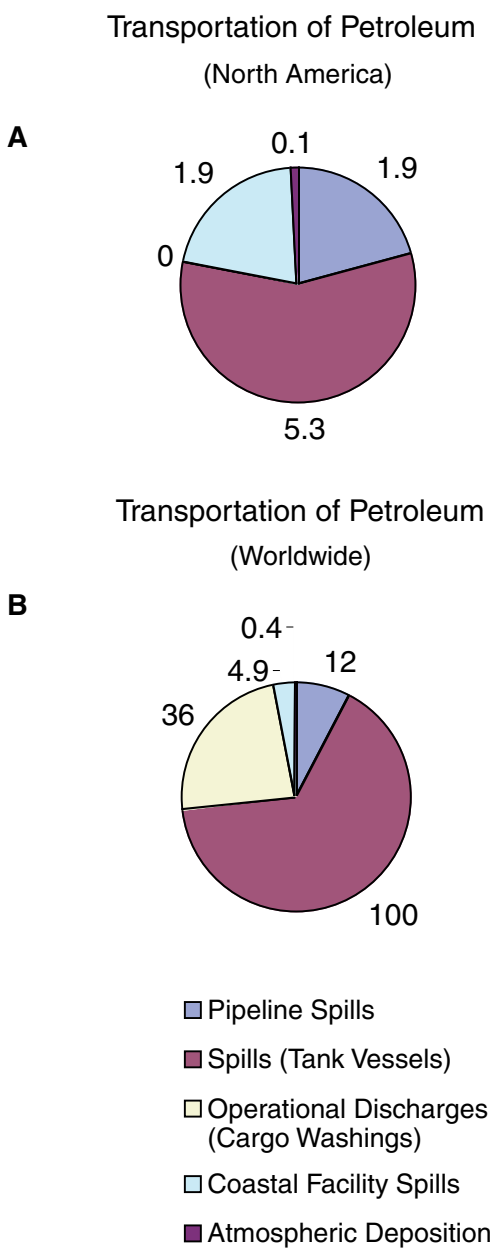

FIGURE 2-7 Relative average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) to North American (A) and worldwide (B) marine environment from sources associated with the transport of petroleum.

ably over the past two decades and now account for only 5,300 tonnes per year, although they are still the dominant source from petroleum transportation activities (Figure 2-7). Tank vessel spills, globally, still discharge some 100,000 tonnes per year of petroleum hydrocarbons into marine waters, and they are the largest input from petroleum transportation worldwide (Table 2-2, Figure 2-7).

Operational Discharges (Cargo Washing)

Tank vessels are permitted discharges related to both cargo and propulsion machinery, whereas nontankers are permitted only machinery-related discharges. Operational discharges from cargo washing are illegal in North American waters. Because of rigorous enforcement and the likelihood that intentional discharges will be detected as spills, no petroleum inputs are estimated for North American waters. Worldwide, operational discharges resulting from cargo washings represent 36,000 tonnes per year (Table 2-2). Increased compliance with international regulations has reduced this amount significantly from past estimates.

Discharges of oil in ballast and tank washing from oil tankers are prohibited within 50 nautical miles of the coast, thus most of the oil inputs from operational tanker discharges occur at sea. These discharges can cause impacts where heavily trafficked shipping lanes pass close to sensitive resources.

Coastal Facilities

Spills from coastal facilities are primarily composed of refined products and account for an estimated 1,900 tonnes per year of petroleum hydrocarbons released to North American waters and 4,900 tonnes worldwide. Coastal pipelines that carry refined products and marine terminals account for 33 percent each of the total discharge. Because of their coastal location, these spills can have significant impacts from both episodic spills and chronic releases.

Atmospheric Deposition (Transportation-related)

Loss of VOC during loading, washing, and transport on tankers contributes the smallest amount of petroleum hydrocarbons to marine waters from transportation activities, both in North America and globally (Figure 2-7). Most of the VOC is methane that enters in the atmosphere and is not counted in the volume entering the sea.

Based on the PAH content of oils spilled and released during shipping, an estimated 170 metric tonnes of PAH are released by transportation. This value does not include combustion-derived PAH produced by ships' power plants that are released to the atmosphere (these contribute to the atmospheric PAH inventory and are included in the atmospheric deposition loadings). PAH release from transportation is approximately 7 percent of the total PAH loading from anthropogenic sources to the North American coastal ocean (Table 2-4). Tank vessel spills account for 70 percent of transportation-related PAH discharges.

The distribution of transportation-related inputs reflects the regions where refinery production and coastal tanker traffic are highest. All of the petroleum inputs into North American waters are point-source spills from pipelines, tank vessels, and coastal facilities, with the exception of a small amount of atmospheric deposition (note that operational discharges from vessels are illegal; thus they are estimated to

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be zero, with illegal discharges reported as spills). A wide range of crude oils and refined products are included in these inputs.

As with spills associated with extraction of petroleum, the impacts from transportation-related spills are very much linked to the spill conditions and location. The release of petroleum over short periods can have significant impacts, depending on the location, time of year, environmental conditions, and effectiveness of containment and recovery actions. Depending on the petroleum type, loss to the atmosphere due to evaporation and volatilization will account for 10 percent (for heavy fuels) to 80 percent (for light, refined products) of the spill volume. The inputs do not account for any oil removal during the response, although recovery of 20 percent of the spill volume is considered to be a good effort. **Much has been learned in the last decade about the fate and effects of oil spills, yet many questions remain, particularly about sub-lethal effects associated with oil residues remaining once cleanup efforts have been terminated.**

Consumption of Petroleum

Once petroleum hydrocarbons have been extracted, transported to refineries, and refined, they are delivered to the consumer. The six major sources of petroleum hydrocarbon releases to the marine environment include land-based sources (river discharge and runoff), two-stroke vessel discharge, non-tank vessel spills (≥100 GT), operational discharges (both ≥ 100 GT and < 100 GT), gross atmospheric deposition, and aircraft dumping. The volumes of oil and other petroleum products from spills or releases associated with consumption dwarf input from all other anthropogenic activities (Figure 2-2A and 2-2B). As mentioned earlier, North America consumes the vast majority of energy worldwide; thus, discharge of by-products from various energy uses remains high for North American waters.

Land-based Sources

Land-based river-runoff discharges are the largest anthropogenic source of petroleum hydrocarbon pollution in the marine environment, accounting for 54,000 tonnes per year in North American waters and 140,000 tonnes worldwide (Table 2-2, Figures 2-9 and 2-10). This input is quite significant because a high percentage is discharged directly into coastal and estuarine waters. Major sources include urban runoff, petroleum refinery wastewater, municipal wastewaters, and non-refining industrial wastes. As the population of coastal regions increase (Fig. 2-11), urban runoff has become more polluted by expansion in the numbers of cars, asphalt-covered highways and parking lots, municipal wastewater loads, and the use and improper disposal of petroleum products.

Recreational Marine Boating

During periods of economic growth in North America, the population spends larger sums of money on recreational marine craft and has more free time to use these small vessels. Recreational use of two-stroke engines in many outboard motors and personal watercraft (e.g., jet skis) has increased significantly during the past two decades. In 1990, heightened awareness of the large numbers and the design inefficiencies of these engines led the U.S. Environmental Protection Agency to begin regulating the "non-road engine" population under the authority of the Clean Air Act. Inputs from use of two-stroke engines in coastal waters are large in areas of high coastal populations. Discharges from two-stroke engines account for an estimated 5,600 tonnes per year into North American waters (data were insufficient for worldwide estimates; Table 2-2, Figure 2-9). The bulk of the input is gasoline, which is thought to rapidly evaporate and volatilize from the water surface. However, very little is known about the actual fate of the discharge. Questions regarding the amount of petroleum residing in the water column or along the surface for biologically significant lengths of time remain. **Together, land-based runoff and discharges by two-stroke engines account for nearly 22 percent of the total petroleum released to the marine environment in North America by all sources (collectively, they represent nearly 64 percent of the total anthropogenic load). This is of particular concern because these discharges occur entirely in coastal environments.**

Non-tank Vessels—Spills and Operational Discharges

Spills from non-tank vessels ≥100 GT represents a relatively small amount of discharge, contributing 1,200 tonnes per year in North America and 7,100 tonnes worldwide (Table 2-2). In contrast, non-tank vessel operational discharges are a major source of petroleum hydrocarbons delivered to global marine waters, which is estimated to be 270,000 tonnes and represents the second highest input of petroleum hydrocarbons into the marine environment (Table 2-2). These sources include machinery space bilge oil, fuel oil sludges, and oily ballast. The International Convention for Prevention of Pollution from Ships (MARPOL 73/78) regulates, worldwide, the design, construction, and operation of commercial vessels of 100 gross tonnes or more, with the goal of reducing or eliminating the discharge of oil and other pollutants into the sea. These regulations have significantly decreased the load, and in 1990, compliance with MARPOL 73/78 ranged from 80 to 99 percent (by class).

Atmospheric Deposition

VOC that enter the marine environment are generated primarily by sources such as internal combustion engines, power generating plants, industrial manufacturing facilities,

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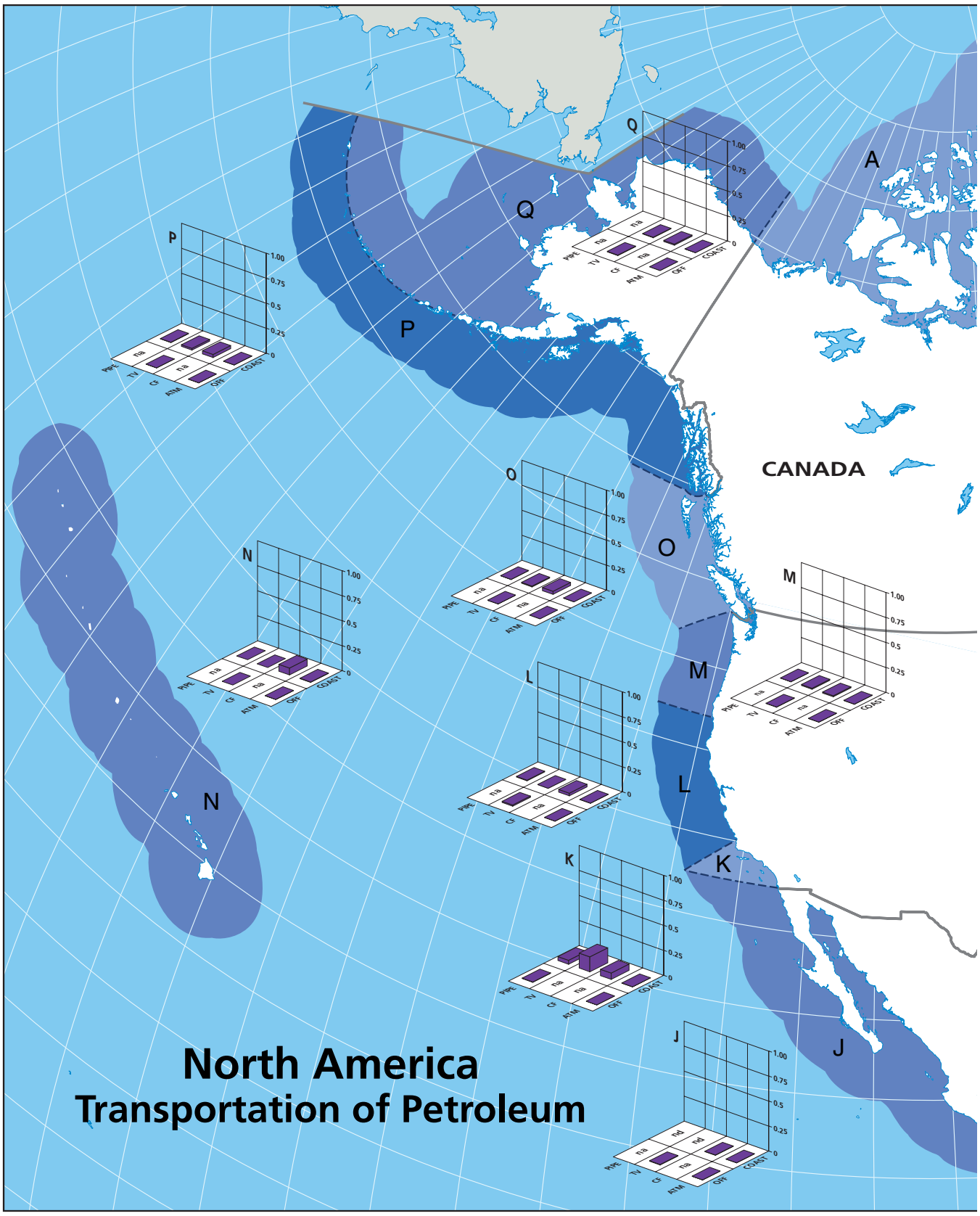

FIGURE 2-8 Geographic variation in average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) to the North American marine environment from sources associated with the transport of petroleum.

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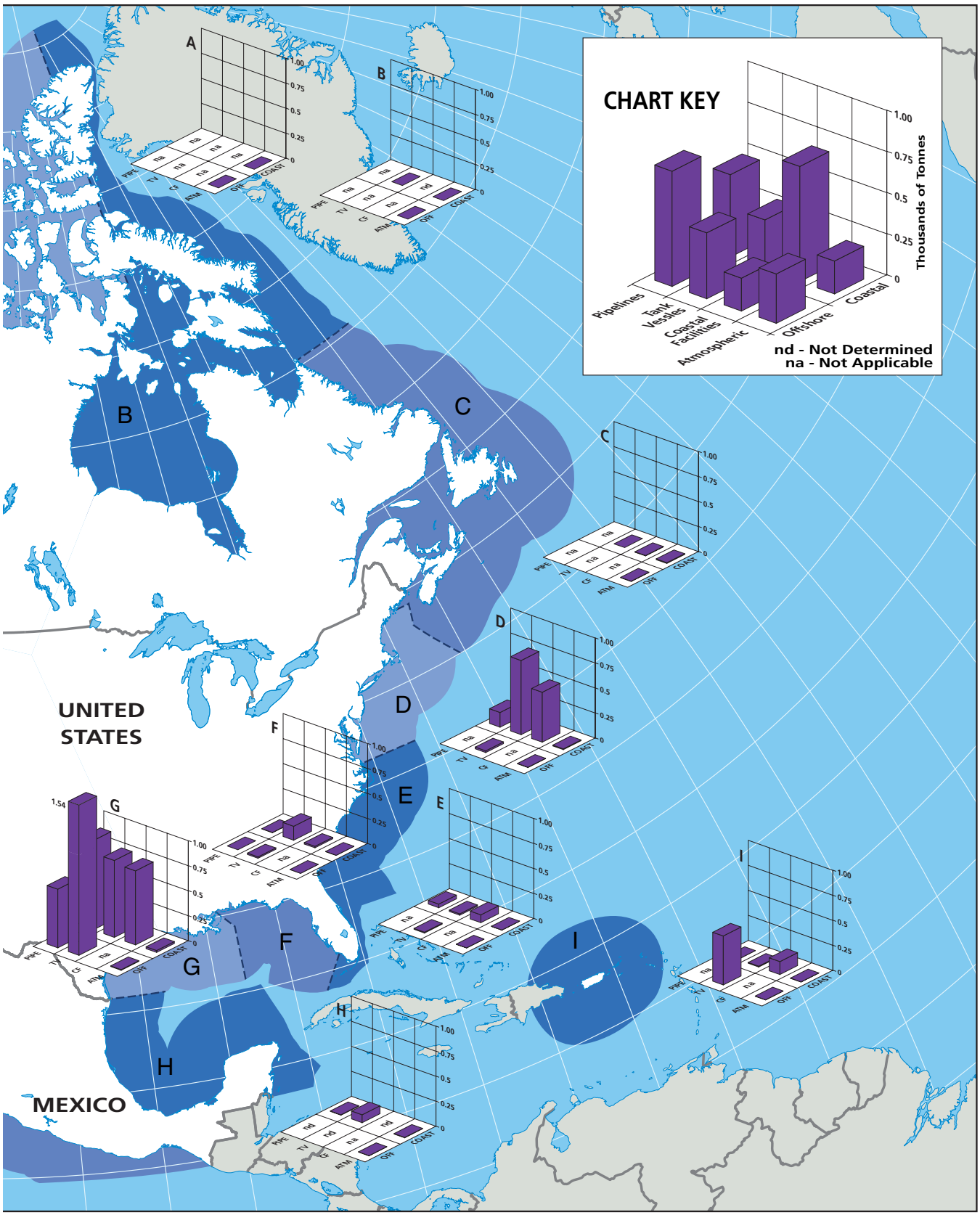

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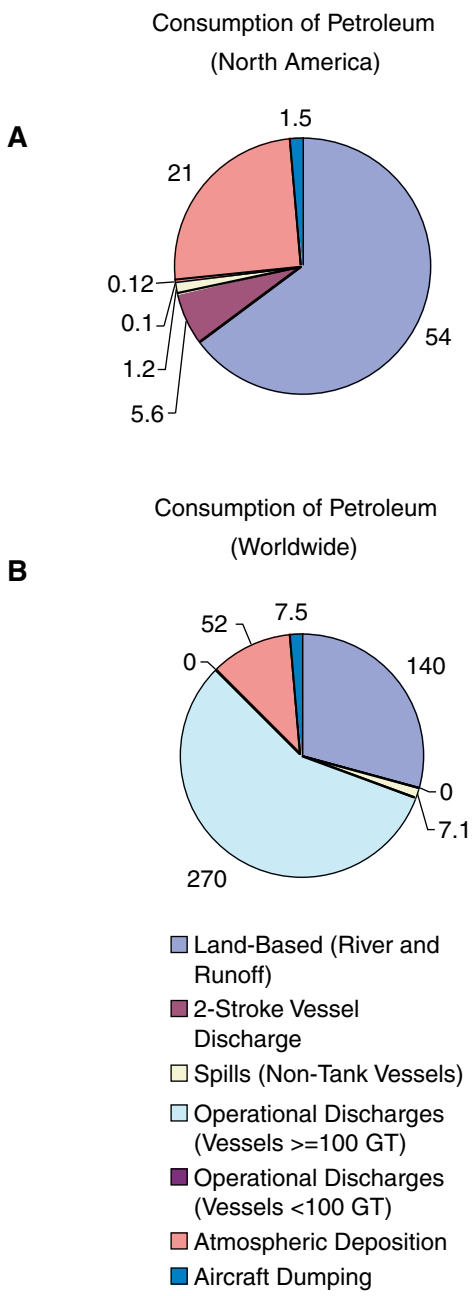

FIGURE 2-9 Relative average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) to North American (A) and worldwide (B) marine environment from sources associated with the consumption of petroleum.

offshore facilities, and marine vessels. Because of their relatively high volatilities and low solubilities, only a small fraction (about 0.2 percent) of VOC released to the marine atmosphere are deposited on the ocean surface. It is estimated that total deposition of petroleum hydrocarbons resulting from VOC release is 21,000 tonnes per year into North American waters and 52,000 tonnes per year, worldwide. The inputs represent estimates of the wet and dry aerosol deposition and gas absorption. Although the net loadings of total petroleum hydrocarbons are negative, due to outgassing of the lighter weight fraction, it is important to note that this category contributes 10 percent of the PAH loadings to the sea. It is difficult to evaluate the impacts, however, because very little is known about the role that air-sea interactions play on the long-term fate of volatile petroleum hydrocarbons. It will be necessary to first obtain a better understanding of the likely concentrations before potential impacts can be evaluated.

Purposeful Jettisoning of Aircraft Fuel

With the expansion of aircraft travel during the past two decades, as well as international flights into and out of North America, the release of unexpended fuel over the coastal ocean has become an increasing source of petroleum hydrocarbons in the marine environment (Table 2-2). The two major sources of aircraft releases are deliberate discharge due to emergency conditions aboard the aircraft (emergency jettisoning) and normal operational releases including the release of partially burned fuel in inefficient engines or inefficient operating modes and the emptying of fuel injection bypass canisters. Modern aircraft have takeoff weights that exceed their landing weights, sometimes by as much as 150 tonnes. Emergency jettisoning of fuel is infrequent but not rare. Reporting such releases is required but is not enforced or monitored. To avoid jettisoning fuel over residential areas, most releases of this type occur over preassigned areas with little human habitation, commonly lakes or coastal waters offshore of coastal airports. It is estimated that 1,500 tonnes of petroleum per year are released over the marine environment in North America and 7,500 tonnes per year worldwide from this source.

Trends in Consumption-Related Inputs

The spatial distribution of consumption-related inputs into North American waters reflects the regions where refinery production and urban areas are highest, namely the northeast corridor, with 39 percent of the consumption-inputs, and the Gulf of Mexico with 16 percent of the consumption-related inputs (see Chapter 3). The distribution also reflects the dominance of land-based inputs into coastal waters.

Over half of the land-based inputs for North America are estimated to occur in the nearshore region between Maine and Virginia, a region rich in estuarine and coastal resources. Land-based sources are generally the largest single source of oil input to the sea for all coastal regions, except for regions with seeps, the Arctic, and the western Pacific. Yet, the long-term fate, bioavailability, and effects of land-based inputs are poorly understood. Assessment of potential impacts is further complicated by the co-occurrence of other contaminants, such as chlorinated hydrocarbons and metals.

Consumption of oil overwhelms all other sources of oil input into coastal waters. Even for offshore waters, consump-

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tion inputs dominate except where seeps occur. It should be noted that the estimates of inputs of the non-point sources have large uncertainties; thus these data indicate only the potential magnitude of the problem.

It is important to note that one of the greatest anthropogenic petroleum hydrocarbon marine polluters is the consumer. Of the total load of petroleum hydrocarbons discharged into the sea, natural seeps account for the largest load, nearly 61 percent of the total. **Of the anthropogenic load, consumers account for nearly 90 percent of the discharge.**

The resulting total estimated loading of PAH to the coastal ocean of North America from all sources is approximately 5,000 tonnes per year. One-half of the PAH loading comes from natural seeps, and atmospheric deposition and land-based sources account for 33 percent and 10 percent of the total PAH loading, respectively. When considering only anthropogenic sources, consumption-related activities contribute an estimated 92 percent of the PAH load. **Extraction and transportation of petroleum contributes a relatively small amount of PAH to the marine environment, especially when compared to the contribution from consumption activities.**

REGIONAL VARIABILITY IN INPUTS OF PETROLEUM AND THEIR SIGNIFICANCE

A major effort of the work on inputs for this report was the spatial allocation of the source loads into regions as well as into coastal and offshore waters. To highlight the differences among the sources by region, the five megaregions (i.e., the Canadian Arctic, the Atlantic coast, the Gulf of Mexico and Puerto Rico, the Pacific coast, and Alaska) are discussed in more detail.

Canadian Arctic

Inputs of petroleum hydrocarbons, in all forms, to the Canadian Arctic are extremely small. The total average annual calculated load to this area, from all sources, during the reporting period (1990-1999) was about 2,300 tonnes (or roughly 1 percent of the total load to North American waters, Table 2-5, Figure 2-12). The dominant source in the area is atmospheric deposition associated with the consumption of petroleum hydrocarbons worldwide. Spills are rare occurrences and are generally associated with tanker traffic in and around the Hudson Bay. Land-based sources make a relatively significant contribution to the coastal zone in areas where development has occurred.

The minimal level of human activity in the Canadian Arctic has resulted in relative small releases of petroleum hydrocarbons to the environment. However, as is discussed in Chapter 5, even a small release during periods of heightened biologic activity (mating, nesting, feeding) at an important site can have long-term impacts on sensitive species. **Continued efforts to reduce spills of all types should be encouraged. In addition, the implications of high-latitude deposition of toxic compounds from diffuse land-based sources (whether transported by river or atmospheric processes) should be investigated.**

Atlantic Seaboard of North America

The Atlantic seaboard extends from northern Canada to Florida. Table 2-6 and Figure 2-13 present the inputs for the Atlantic regions by source and location. It is very clear that consumption sources dominate the inputs and the region from Maine to Virginia has the greatest loads along the Atlantic coast. This one region has 54 percent of all the estimated land-based inputs for North America. It has the second highest inputs from recreational marine vessels. It also ranks third out of seventeen regions for inputs from tank vessel spills, with 38 percent of the inputs into coastal waters, and fourth in terms of facility spills, with nearly 30 percent of the coastal inputs. A large coastal population, high degree of urbanization, and high energy demand all contribute to these large inputs from both transportation and consumption sources. With little oil and gas production, inputs into offshore waters are dominated by atmospheric deposition. Aircraft dumping is another significant input into offshore waters along the Atlantic regions.

The elevated inputs of petroleum hydrocarbon as total petroleum hydrocarbons (TPH) and PAH, due to human activities in this portion of North America, and especially the load entering the coastal zone from land-based sources, suggest that the sensitive marine communities in these areas are at significant risk from chronic releases, as well as the long-term, sublethal exposure associated with them. The ultimate effect of this exposure remains an area of important scientific research, but greater understanding and monitoring of nonpoint sources of petroleum pollution is needed in these areas.

Gulf of Mexico and Puerto Rico

Inputs to the Gulf of Mexico and Puerto Rico are presented in Table 2-7 and Figure 2-14, and have a very different mix and loads of sources for coastal and offshore waters. Offshore, seeps dominate inputs in the Gulf of Mexico. For anthropogenic sources, the largest offshore source varies by region: around Puerto Rico and eastern Gulf of Mexico it is spills from tank vessels; in the western Gulf of Mexico it is produced water discharges followed closely by tank vessel spills; in Mexico, it is produced water. In coastal areas, once again land-based sources dominate in all regions. Despite including the Mississippi River discharge and a high concentration of coastal refineries, the western Gulf of Mexico received only 21 percent of the total inputs from land-based sources in North America. Transportation-related inputs to the western Gulf of Mexico were about 15-25 times greater than the other Gulf and Caribbean regions, and equally di-

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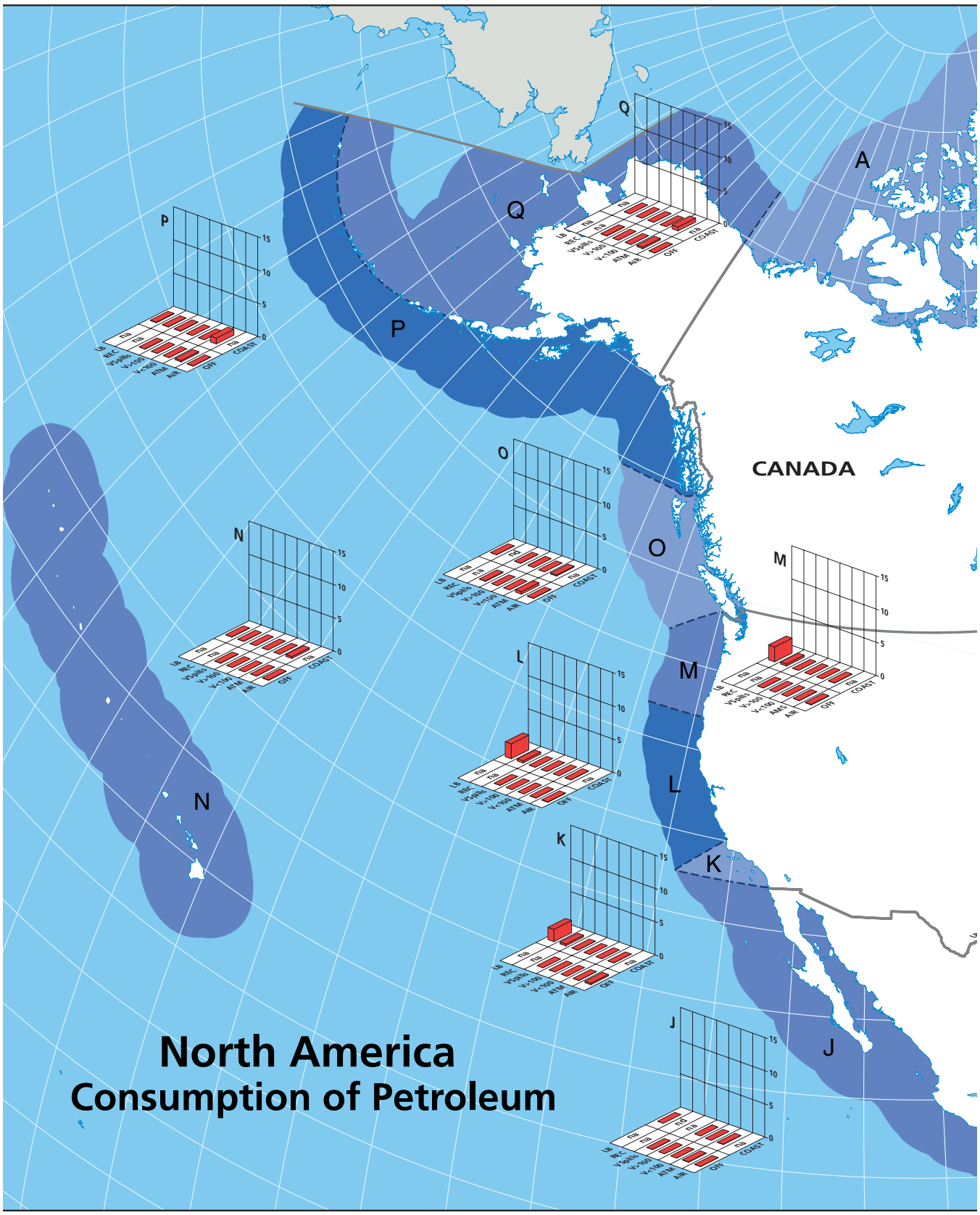

FIGURE 2-10 Geographic variation in average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) to the North American marine environment from sources associated with the consumption of petroleum.

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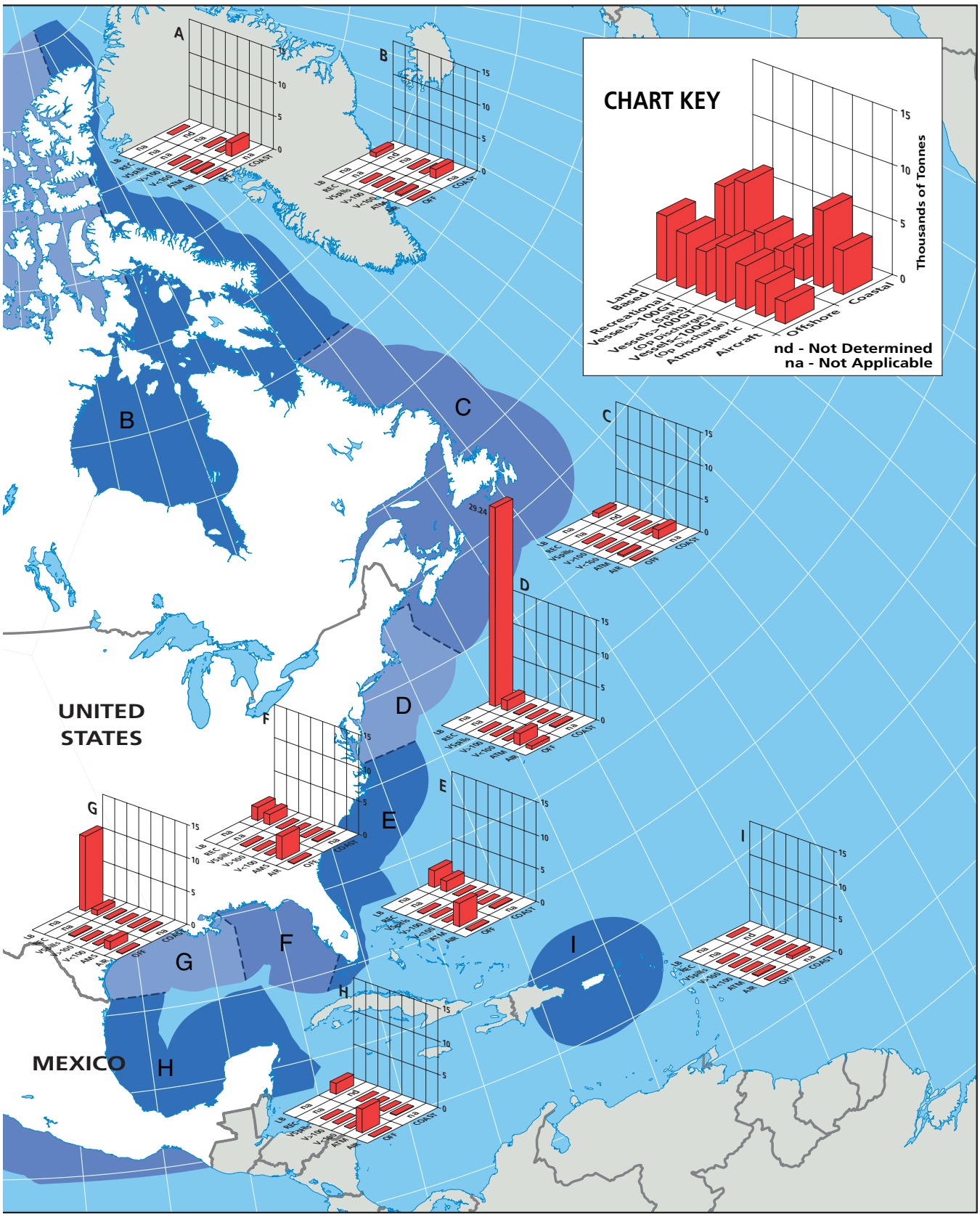

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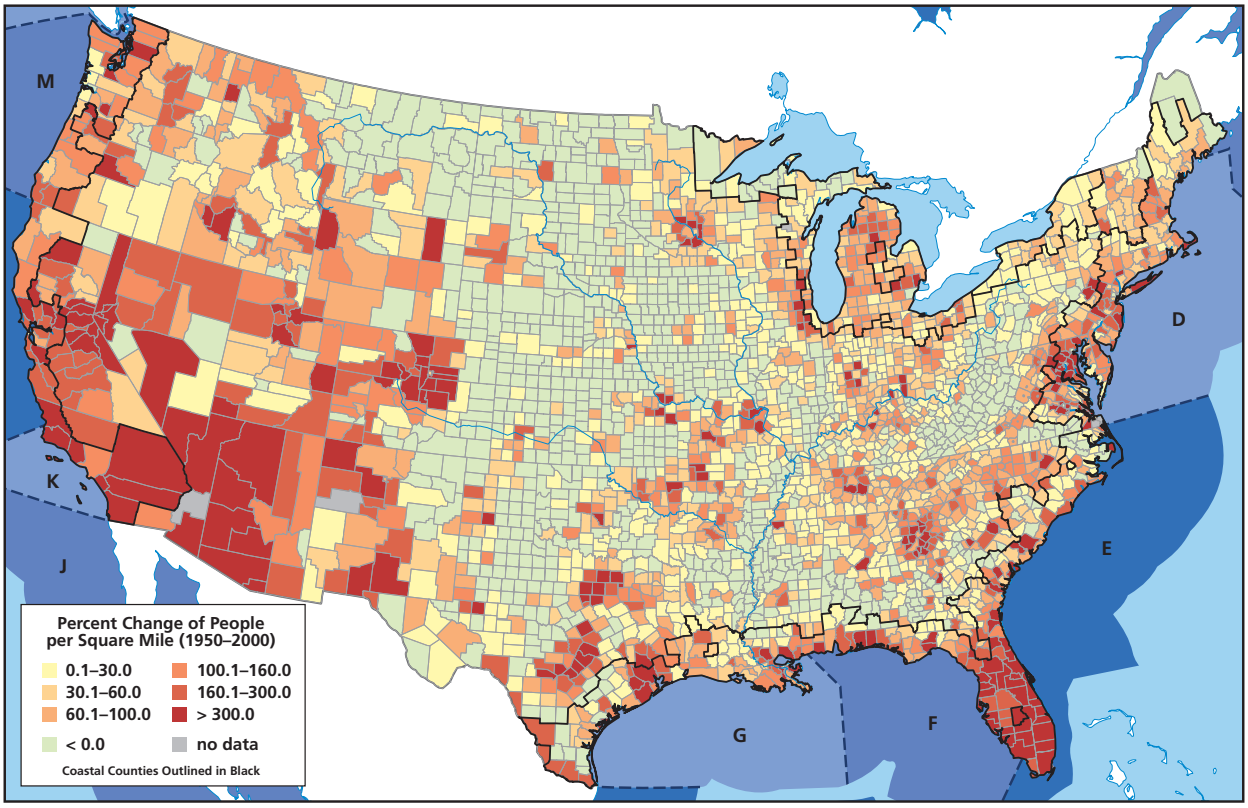

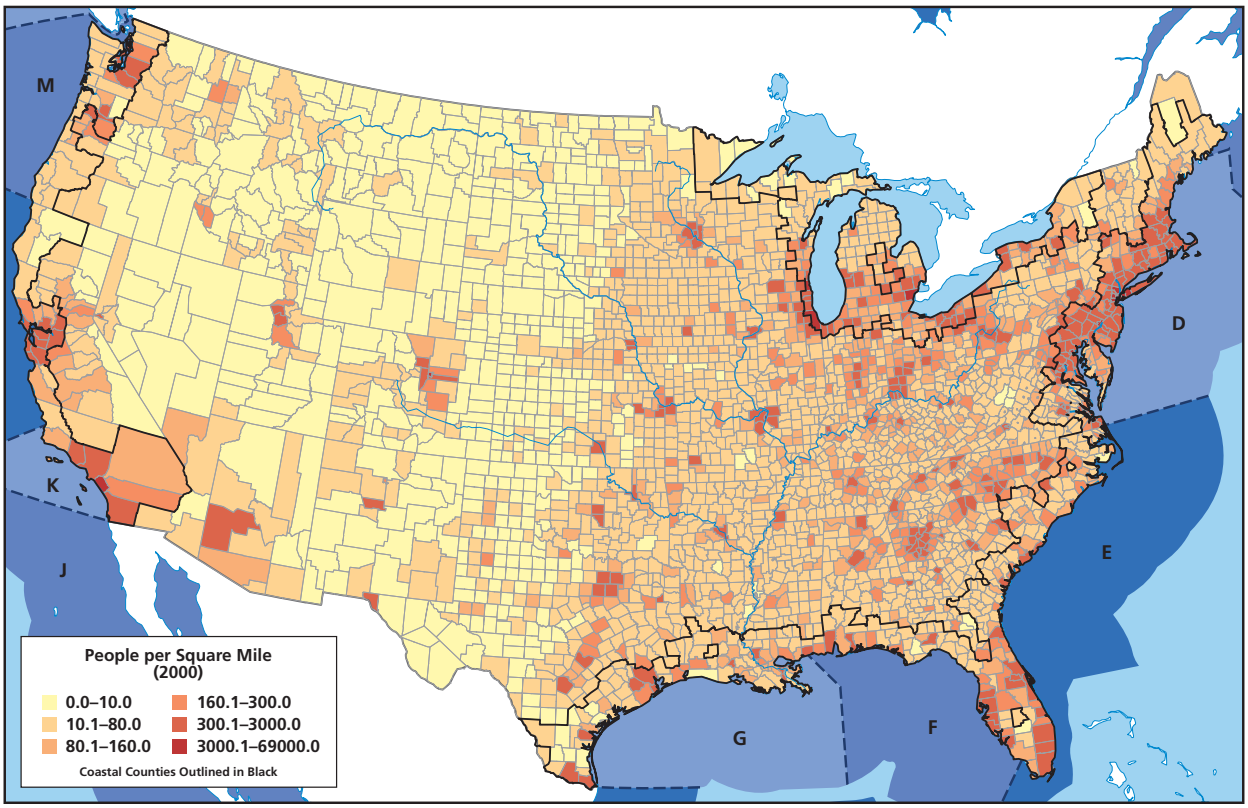

FIGURE 2-11 The migration to the coast, clearly demonstrated in changes in population density (a) over the latter half of the 20th century, has led to high coastal populations (b) in the United States and elsewhere. (Data provided by U.S. Bureau of the Census.)

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vided among coastal pipelines, tanker spills, and coastal facilities. These sources reflect the large petroleum industry of the region that involves all phases of oil and gas exploration, production, and transportation.

Spills from pipelines and tank vessels into the Western Gulf of Mexico release about 1,600 tonnes into both offshore and coastal areas, thus continued efforts by the transportation industries is needed to reduce the threat posed by such spills. In addition to the direct threat posed from spills, the elevated inputs of petroleum hydrocarbon (both as TPH and as PAH) due to human activities within the Mississippi River watershed and along the Gulf Coast, especially that load entering the coastal zone from land-based sources, suggests that sensitive marine communities in these areas are at a significant risk from chronic releases and the long-term, sublethal exposure associated with them. As discussed earlier, the ultimate effect of this exposure remains an area of important scientific research, but greater understanding and monitoring of nonpoint sources of petroleum pollution is needed in these areas.

Pacific Seaboard of North America and Hawaii

The total average annual input of petroleum hydrocarbons to the Pacific seaboard of North America (including Hawaii) on a regional basis, is relatively low. This area, the largest of the five discussed, receives roughly 31,000 tonnes of petroleum hydrocarbons from all sources each year (less than 10 percent on the total annual load to North American waters; Table 2-8, Figure 2-15). The dominant source of petroleum hydrocarbons to the coastal zone is from consumption related activities, and as expected, these loads show marked correlation to the distribution of human population and the degree of urbanization. In addition, the heavy use of recreational marine vessels in some regions results in substantial loads of petroleum hydrocarbons, accounting for nearly 50 percent of the calculated load for waters off California. Offshore, inputs are much smaller, with the significant exception of offshore Southern California. Here the extensive system of natural seeps off Coal Oil Point release approximately 20,000 tonnes of crude petroleum to the marine environment each year (accounting for nearly two thirds of the total load received by coastal and offshore waters of the Pacific seaboard, including Hawaii).

The load from consumption-related activities to coastal waters off more densely populated coastal regions of western North America may represent a significant risk to natural resources in these areas, depending on local oceanographic conditions (see Chapter 4) and the nature of the biota. This risk may be even more significant if these ecosystems should prove sensitive to chronic exposure to certain toxins found in petroleum hydrocarbons (such as PAH; see Chapter 5). Spills, although infrequent compared to some regions, can still be significant, especially if they occur at important periods of biologic activity or in particularly important locations.

TABLE 2-5 Average Annual Input (1990-1999) of Petroleum Hydrocarbons (tonnes) for the Canadian Arctic

ZONE (Coastal)		**A**	**B**
Sum Seeps[a]		**na**	**na**
	Platforms	na	na
	Atmospheric	na	na
	Produced	na	na
Sum Extraction[b]		**na**	**na**
	Pipelines	na	na
	Tank vessel	na	trace[c]
	Coastal facilities	na	na
	Atmospheric[d]	trace	trace
Sum Transportation		**trace**	**trace**
	Land-based	trace[e]	660
	Recreational vessels	nd[f]	nd
	Vessels >100GT (spills)	0[g]	0
	Vessel >100GT (op discharge)	trace	trace
	Vessel <100GT (op discharge)	trace	trace
	Atmospheric	2000	1300
	Aircraft[h]	na	na
Sum Consumption		**2000**	**2000**
ZONE (Offshore)		**A**	**B**
Sum Seeps[a]		**na**	**na**
	Platforms	na	na
	Atmospheric	na	na
	Produced	na	na
Sum Extraction		**na**	**na**
	Pipelines	na	na
	Tank vessel	na	na
	Atmospheric[d]	trace	trace
Sum Transportation[b]		**trace**	**trace**
	Land-based[i]	na	na
	Recreational vessels[j]	na	na
	Vessels >100GT (spills)	na	trace
	Vessel >100GT (op discharge)	trace	trace
	Vessel <100GT (op discharge)	trace	trace
	Atmospheric	220	230
	Aircraft	20	50
Sum Consumption		**240**	**270**
Grand Total		**2300**	**2300**
Sum of Anthropogenic		**2300**	**2300**

[a]No known seeps in these regions
[b]No known oil and gas production in these regions
[c]Estimated loads of less than 10 tonnes per year reported as "trace"
[d]Small number of tankers carrying fuel to coastal areas assumed
[e]Pristine waters in this region assumed to carry some fraction of petroleum bearing sediment eroded from exposed sources rocks (see Chapter 3 and Appendix I)
[f]Populations of recreational vessels were not available for these regions (see Chapter 3 and Appendix F)
[g]No spills from vessels greater than 100 GT were reported in these regions for the reporting period (see Chapter 3 and Appendix E)
[h]Purposeful jettisoning of fuel not allowed within 3 nmiles of land (see Chapter 3 and Appendix E)
[i]Land-based inputs are defined in this study as being limited to the coastal zone (see Chapter 3 and Appendix I)
[j]Recreational vessels are defined in this study as being limited to operations within 3 miles of the coast (see Chapter 3 and Appendix F)

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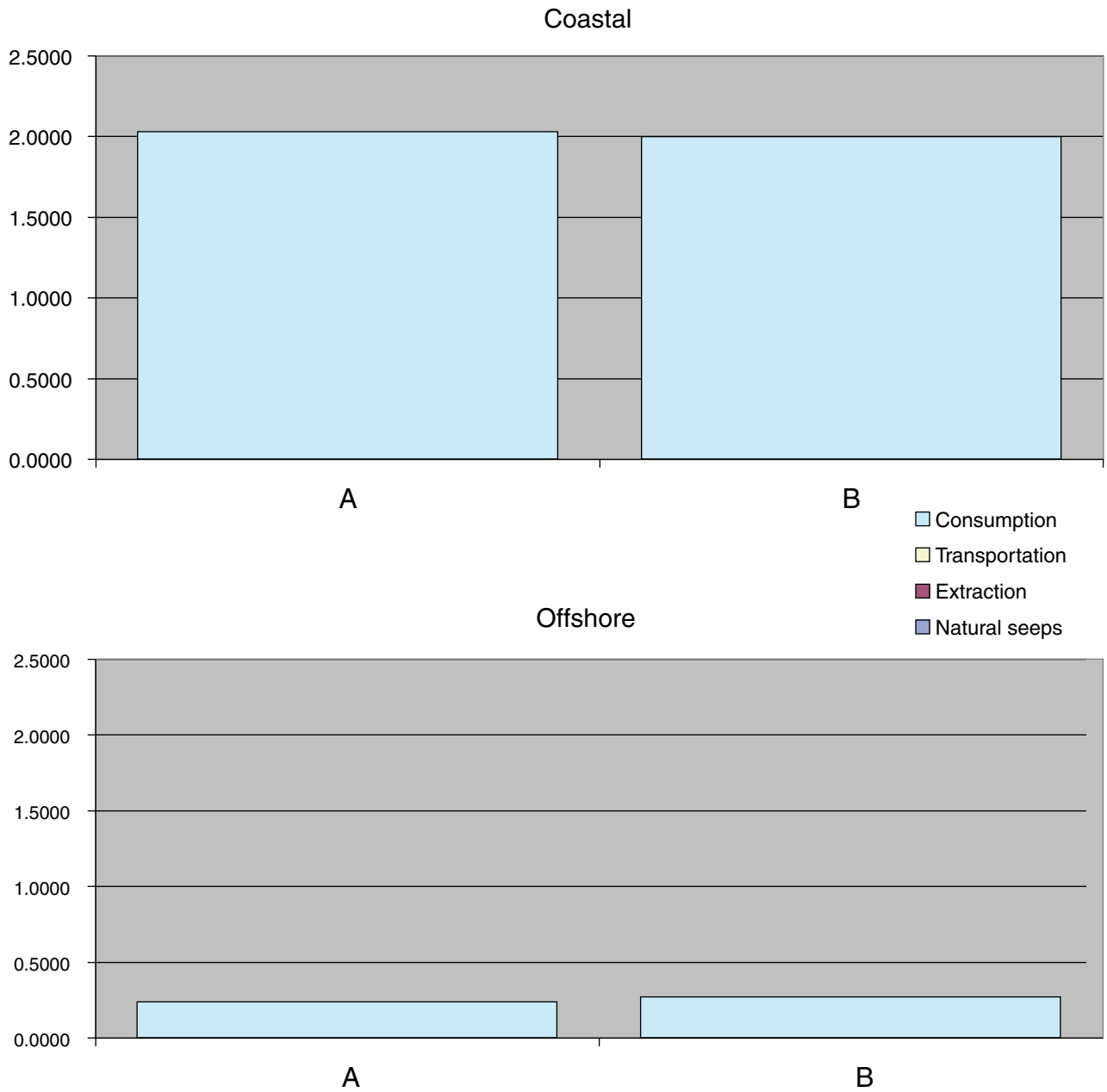

FIGURE 2-12 Average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) for the Canadian Arctic.

Effort to reduce the frequency and size of such spills should continue to be undertaken.

Alaska

Alaska was divided into two regions, divided by the Aleutian Islands. Inputs to these regions are presented in Table 2-9 and Figure 2-16, showing dramatically different sources and loads for coastal and offshore waters. Surprisingly, aircraft dumping is estimated to be one of the largest sources of oil into offshore areas, and inputs from spills from non-tank vessels are small but one-two orders of magnitude greater than spills from tankers. In coastal waters, seeps in south-central Alaska are responsible for over 40 percent of the calculated inputs[3] during the reporting period (1990-1999; Table 2-9).

[3]As discussed in Chapter 3 and Appendix I, erosion of organic rich source rocks can yield petroleum-bearing sediment in locally significant amounts. However, this material is largely bound within sediment particles, thus suggesting it is largely not biologically available.

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TABLE 2-6 Average Annual Input (1990-1999) of Petroleum Hydrocarbons (tonnes) for Atlantic Seaboard of North America

ZONE (Coastal)		C	D	E
Sum Seeps[a]		**na**	**na**	**na**
	Platforms	nd[b]	trace[c]	na
	Atmospheric	nd[b]	trace	na
	Produced	nd[b]	trace	na
Sum Extraction		**nd**[b]	**trace**	**na**[d]
	Pipelines	0	150	36
	Tank vessel	0	740	14
	Coastal facilities	trace	500	79
	Atmospheric	trace	trace	trace
Sum Transportation		**11**	**1400**	**130**
	Land-based	500	29000	2500
	Recreational vessels	nd	1500	1600
	Vessels >100GT (spills)	trace	88	22
	Vessel >100GT (op discharge)	trace	trace	trace
	Vessel <100GT (op discharge)	trace	19	trace
	Atmospheric	93	160	120
	Aircraft[e]	na	na	na
Sum Consumption		**1400**	**31000**	**4200**
ZONE (Offshore)		**C**	**D**	**E**
Sum Seeps		**na**	**na**	**na**
	Platforms	28[a]	na	na
	Atmospheric	trace	na	na
	Produced	62	na	na
Sum Extraction		**90**	**na**[d]	**na**[d]
	Pipelines	na	na	na
	Tank vessel	na	17	trace
	Atmospheric	trace[f]	trace	trace
Sum Transportation		**trace**	**19**	**trace**
	Land-based[g]	na	na	na
	Recreational vessels[h]	na	na	na
	Vessels >100GT (spills)	trace	trace	40
	Vessel >100GT (op discharge)	trace	17	trace
	Vessel <100GT (op discharge)	trace	trace	trace
	Atmospheric	160	1700	3500
	Aircraft	120	525	90
Sum Consumption		**290**	**2300**	**3600**
Grand Total		**1800**	**34000**	**8000**
Sum of Anthropogenic		**1800**	**34000**	**8000**

[a]No known seeps in these regions

[b]All oil production is offshore; so, it is assumed that all releases are to offshore waters.

[c]Estimated loads of less than 10 tonnes per year reported as "trace"

[d]No known oil and gas production in this region.

[e]Purposeful jettisoning of fuel not allowed within 3 nmiles of land (see Chapter 3 and Appendix F)

[f]Small number of tankers carrying fuel to coastal areas assumed

[g]Land-based inputs are defined in this study as being limited to the coastal zone (see Chapter 3 and Appendix I)

[h]Recreational vessels are defined in this study as being limited to operations within 3 miles of the coast (see Chapter 3 and Appendix F)

Alaska represents a unique challenge to understanding petroleum hydrocarbons in the marine environment. Anthropogenic sources of petroleum hydrocarbons are dominated by spills occurring during the extraction or transportation of petroleum. Unlike regions that have undergone a greater degree of urbanization, low-level, chronic releases of petroleum are not significant in Alaska, thus the erosion of petroleum-bearing rock can be significant at a local scale. Conversely, the ecosystems in the coastal and offshore areas of Alaska have had no need to adapt to elevated concentrations of petroleum hydrocarbon and may, therefore, be even more sensitive to future exposures. Continued efforts by the extraction and transportation industries to minimize the potential for spills will be a key component to ensure the health of natural resources in this area.

SUMMARY OF MAJOR FINDINGS AND RECOMMENDATIONS

In addition to the general conclusions discussed above, several specific actions have to be taken to address the issues raised in this report (see Chapters 3, 4, and 5 for greater detail). This study was largely funded by U.S. entities, especially federal agencies. Many of the following recommendations are therefore focused on actions that can be taken by the United States. This does not mean, however, that they are not broadly applicable to the international community. On the contrary, both individual nations and groups of nations should consider how these recommendations could be implemented worldwide.

Inputs

Diffuse sources (natural seeps and runoff from land-based sources) are responsible for the majority of petroleum hydrocarbon inputs into North American waters, with contributions of 61 percent and 21 percent, respectively. In contrast, discharges from extraction and marine transportation of petroleum are responsible for less than 3 percent of the hydrocarbon inputs. Natural seeps represent the largest single petroleum hydrocarbon input but there is a great range in the uncertainty estimation. **Federal agencies especially the U.S. Geological Survey (USGS), the Minerals Management Service (MMS), and the National Oceanic and Atmospheric Administration (NOAA) should work to develop more accurate techniques for estimating inputs from natural seeps, especially those adjacent to sensitive habitats.** Likely techniques will include remote sensing and ground truthing. This will aid in distinguishing the effects of natural processes from those of anthropogenic activities.

Urban runoff and recreational boating require attention because the spills are chronic and often occur in sensitive ecosystems. For example, the range of uncertainty in estimates of land-based petroleum hydrocarbons is four orders

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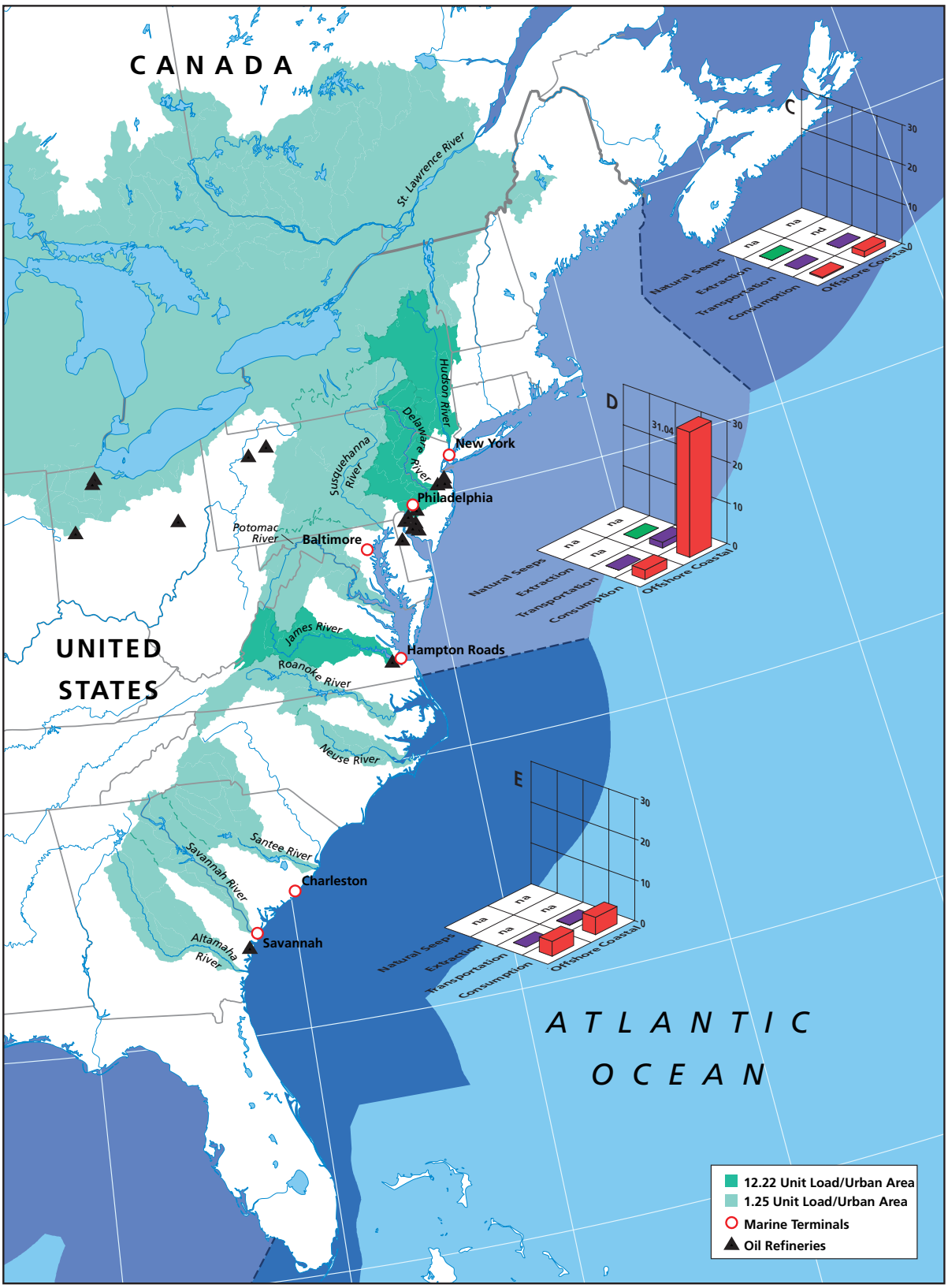

FIGURE 2-13 Average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) for Atlantic Seaboard of North America. (Additional data provided by EIA, EPA, USGS, and U.S. Coast Guard.)

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TABLE 2-7 Average Annual Input (1990-1999) of Petroleum Hydrocarbons (tonnes) for the Gulf of Mexico and Puerto Rico

ZONE (Coastal)	F	G	H	I
Sum Seeps[a]	**na**	**na**	**na**	**na**
Platforms	trace[b]	90	nd[c]	na
Atmospheric	trace	trace	nd[c]	na
Produced	trace	590	trace	na
Sum Extraction	**trace**	**680**	**trace[c]**	**na[d]**
Pipelines	trace	890	trace	trace
Tank vessel	140	770	80	trace
Coastal facilities	10	740	nd[e]	130
Atmospheric	trace	trace	trace	trace
Sum Transportation	**160**	**2400**	**90**	**130**
Land-based	1600	11000	1600	trace[f]
Recreational vessels	770	770	nd[g]	nd[g]
Vessels >100GT (spills)	30	100	trace	trace
Vessel >100GT (op discharge)	trace	trace	trace	trace
Vessel <100GT (op discharge)	trace	trace	trace	trace
Atmospheric	60	90	100	50
Aircraft[h]	na	na	na	na
Sum Consumption	**2500**	**12000**	**1700**	**50**

ZONE (Offshore)	F	G	H	I
Sum Seeps	**70000**	**70000**	**na[a]**	**na[a]**
Platforms	trace	50	61c	na
Atmospheric	trace	60	40	na
Produced	trace	1700	130	na
Sum Extraction	**trace**	**1800**	**231**	**na[d]**
Pipelines	trace	60	nd[i]	na
Tank vessel	10	1500	nd[i]	490
Atmospheric	trace	trace	trace	trace
Sum Transportation	**10**	**1600**	**trace**	**490**
Land-based[j]	na	na	na	na
Recreational vessels[k]	na	na	na	na
Vessels >100GT (spills)	70	120	trace	10
Vessel >100GT (op discharge)	trace	25	trace	trace
Vessel <100GT (op discharge)	trace	trace	trace	trace
Atmospheric	1600	1200	3600	70
Aircraft	80	80	20	20
Sum Consumption	**1800**	**1400**	**3600**	**100**
Grand Total	**74000**	**91000**	**5600**	**790**
Sum of Anthropogenic	**4400**	**21000**	**5600**	**790**

[a]No known seeps in these regions
[b]Estimated loads of less than 10 tonnes per year reported as "trace"
[c]Lack of precise locations for platforms in this zone precluded determining whether spills or other releases occurred less than 3 nmiles from shore (see Chapter 3 and Appendix D). Thus, all values for this zone reported as "offshore."
[d]No known oil and gas production in this region
[e]No information on the existence of coastal facilities was available for this region (see Chapter 3 and Appendix G).
[f]Insufficient water quality data exist to calculate input in this region, but existence of some urban landscape suggests it is a non-zero number (see Chapter 3 and Appendix I).
[g]Populations of recreational vessels were not available for these regions (see Chapter 3 and Appendix F)
[h]Purposeful jettisoning of fuel not allowed within 3 nmiles of land (see Chapter 3 and Appendix E)
[i]No information on transportation-related spills was available for this region (see Chapter 3 and Appendixes D, E, and G)
[j]Land-based inputs are defined in this study as being limited to the coastal zone (see Chapter 3 and Appendix I)
[k]Recreational vessels are defined in this study as being limited to operations within 3 miles of the coast (see Chapter 3 and Appendix F)[1]

of magnitude, and the upper limit, if reasonable, would dominate all other inputs. This uncertainty reflects a variety of limitations, including a lack of adequate background data. **To refine estimates associated with non-point sources, Federal agencies, especially EPA and the USGS, should work with state and local authorities to routinely collect and share data on the concentration of petroleum hydrocarbons in major river outflows and harbors in storm- and wastewater streams.**

The estimates presented here demonstrate the important role of air-sea exchange of hydrocarbons in (1) the persistence of petroleum hydrocarbons in surface waters and (2) the potential degradation of coastal air quality. These estimates are limited both by the lack of detailed field measurements of hydrocarbons in seawater and the coastal atmosphere under a variety of conditions and by the relatively poor knowledge of the fundamental physics of air-sea exchange. Directed research is needed that (1) conducts specific coupled field studies of air-sea interaction and (2) applies these studies to the modeling of petroleum hydrocarbon exchange at regional and global scales. On-going and growing investigations of air-sea exchange of carbon dioxide, conducted to better understand global climate change, provide a significant opportunity to improve the estimates of petroleum hydrocarbon exchange between the atmosphere and the surface ocean.

During 1990-1999, spillage from vessels in U.S. waters was less than 40 percent of that during the prior decade, and it now represents less than 2 percent of the petroleum hydrocarbon inputs into North American waters. Significant reductions in spillage were also realized worldwide. Improvements in vessel operation and design and the introduction of related federal and international regulations contributed to this decline in oil spills. In U.S. marine waters, the largest spills come from vessels, followed by pipelines and facilities. Vessels have produced 109 spills of greater than 34 tonnes (10,000 gallons) in size since 1990, and these larger spills had an average size of about 400 tonnes. During the 1990s, tanker vessels were responsible for about 89 percent of the spillage from vessels. The comprehensive port control regime, administered by the U.S. Coast Guard, cooperative programs with ship owners and the boating community, and active participation of the International Maritime Organization in developing effective international regulatory standards have contributed to the decline in oil spills and operational discharges. **These efforts and relationships should be continued and further strengthened where appropriate.**

Estimated operational discharges from vessels contribute very significant inputs. More than 99 percent of the estimated volume of operational discharge is related to non-compliance, because existing regulations restrict operational discharges of oil or limit them to not more than 15 ppm. The extent of non-compliance is difficult to assess, and therefore these estimates have a high level of uncertainty. **Federal**

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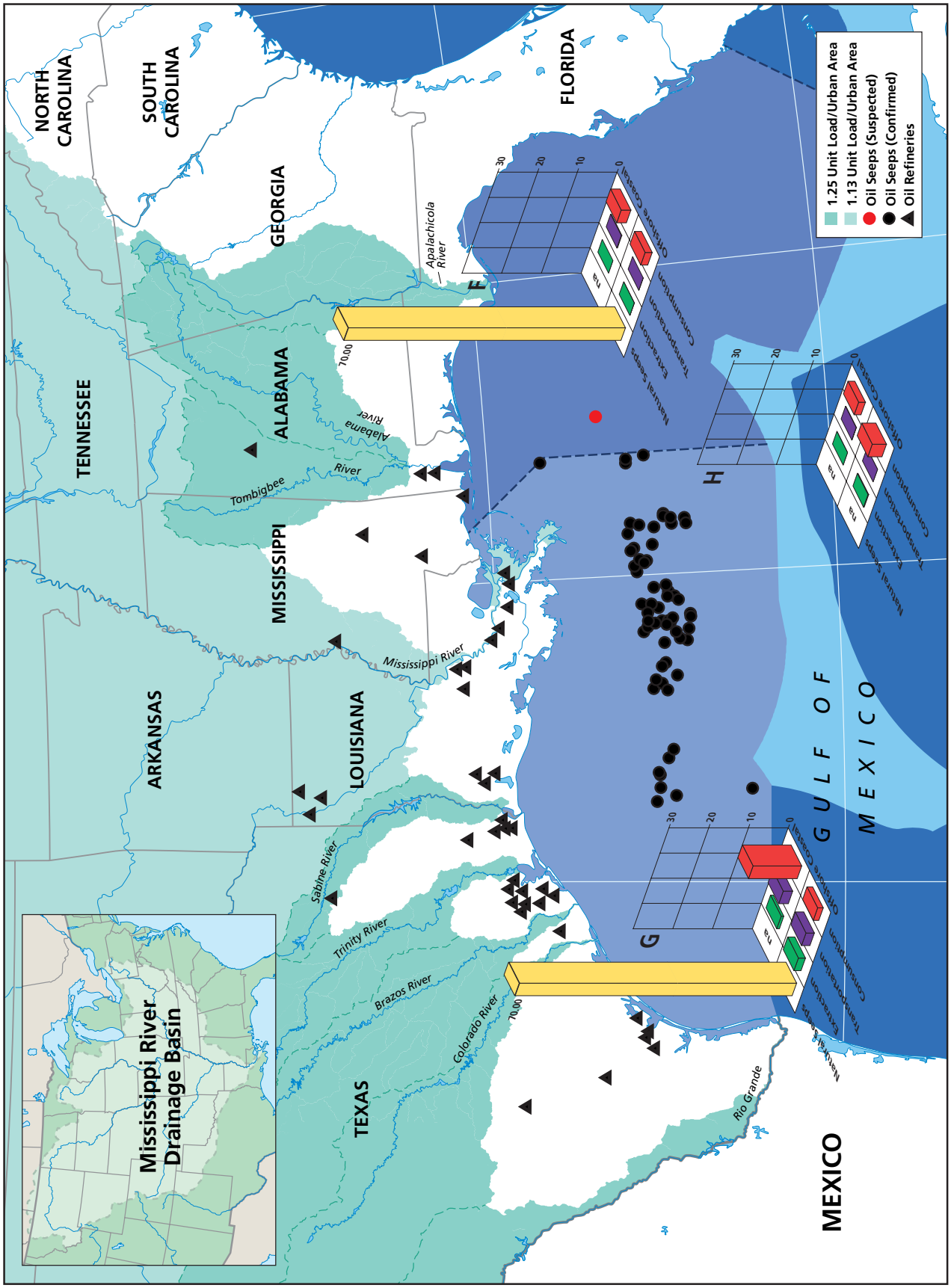

FIGURE 2-14 Average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) for the Gulf of Mexico and Puerto Rico. (Additional information provided by EIA, USGS, EPA, and McGraw Hill Higher Education.)

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TABLE 2-8 Average Annual Input (1990-1999) of Petroleum Hydrocarbons (tonnes) for the Pacific Seaboard of North America (plus Hawaii)

ZONE (Coastal)		**J**	**K**	**L**	**M**	**N**	**O**
Sum Seeps[a]		**na**	**na**	**na**	**na**	**na**	**na**
	Platforms	na	trace[b]	trace	na	na	na
	Atmospheric	na	trace	na	na	na	na
	Produced	na	trace	na	na	na	na
Sum Extraction		**na**[c]	**trace**	**trace**	**na**[c]	**na**[c]	**na**[c]
	Pipelines	nd[d]	39	trace	trace	trace	0
	Tank vessel	nd	150	trace	10	trace	0
	Coastal facilities	trace	62	26	10	31	69
	Atmospheric	trace	trace	trace	trace	trace	trace
Sum Transportation		**trace**	**250**	**35**	**23**	**42**	**73**
	Land-based	860	1900	2300	1600	29	65
	Recreational vessels	nd[e]	280	320	1600	36	nd
	Vessels >100GT (spills)	nd[f]	28	trace	35	26	trace
	Vessel >100GT (op discharge)	trace	trace	trace	trace	trace	trace
	Vessel <100GT (op discharge)	trace	trace	trace	trace	trace	trace
	Atmospheric	420	14	44	120	150	280
	Aircraft[g]	na	na	na	na	na	na
Sum Consumption		**1300**	**2200**	**2700**	**3400**	**240**	**350**
ZONE (Offshore)		**J**	**K**	**L**	**M**	**N**	**O**
Sum Seeps		**na**	**20000**	**na**	**na**	**na**	**na**
	Platforms	na	trace	na	na	na	na
	Atmospheric	na	trace	na	na	na	na
	Produced	na	85	na	na	na	na
Sum Extraction		**na**[c]	**92**	**na**[c]	**na**[c]	**na**[c]	**na**[c]
	Pipelines	nd[h]	trace	0	0	0	0
	Tank vessel	trace	0	12	trace	trace	0
	Atmospheric	trace	trace	trace	trace	trace	trace
Sum Transportation		**trace**	**trace**	**12**	**trace**	**trace**	**trace**
	Land-based[i]	na	na	na	na	na	na
	Recreational vessels[j]	na	na	na	na	na	na
	Vessels >100GT (spills)	trace	trace	16	13	87	52
	Vessel >100GT (op discharge)	trace	trace	trace	trace	trace	trace
	Vessel <100GT (op discharge)	trace	trace	trace	trace	trace	trace
	Atmospheric	140	na	40	33	390	38
	Aircraft	15	230	75	30	45	75
Sum Consumption		**160**	**240**	**130**	**82**	**520**	**170**
Grand Total		**1500**	**23000**	**2800**	**3500**	**700**	**590**
Sum of Anthropogenic		**1500**	**2100**	**2800**	**2100**	**700**	**590**

[a]No known seeps in these regions
[b]Estimated loads of less than 10 tonnes per year reported as "trace"
[c]No known oil and gas production in this region
[d]No information on transportation-related spills was available for this region (see Chapter 3 and Appendixes D, E, and G)
[e]Populations of recreational vessels were not available for these regions (see Chapter 3 and Appendix F)
[f]Insufficient information on spills from cargo vessels was available for this region (see Chapter 3 and Appendix E)
[g]Purposeful jettisoning of fuel not allowed within 3 nmiles of land (see Chapter 3 and Appendix E)
[h]Insufficient information on spills from pipelines was available for this region (see Chapter 3 and Appendix E)
[i]Land-based inputs are defined in this study as being limited to the coastal zone (see Chapter 3 and Appendix I)
[j]Recreational vessels are defined in this study as being limited to operations within 3 nmiles of the coast (see Chapter 3 and Appendix F)

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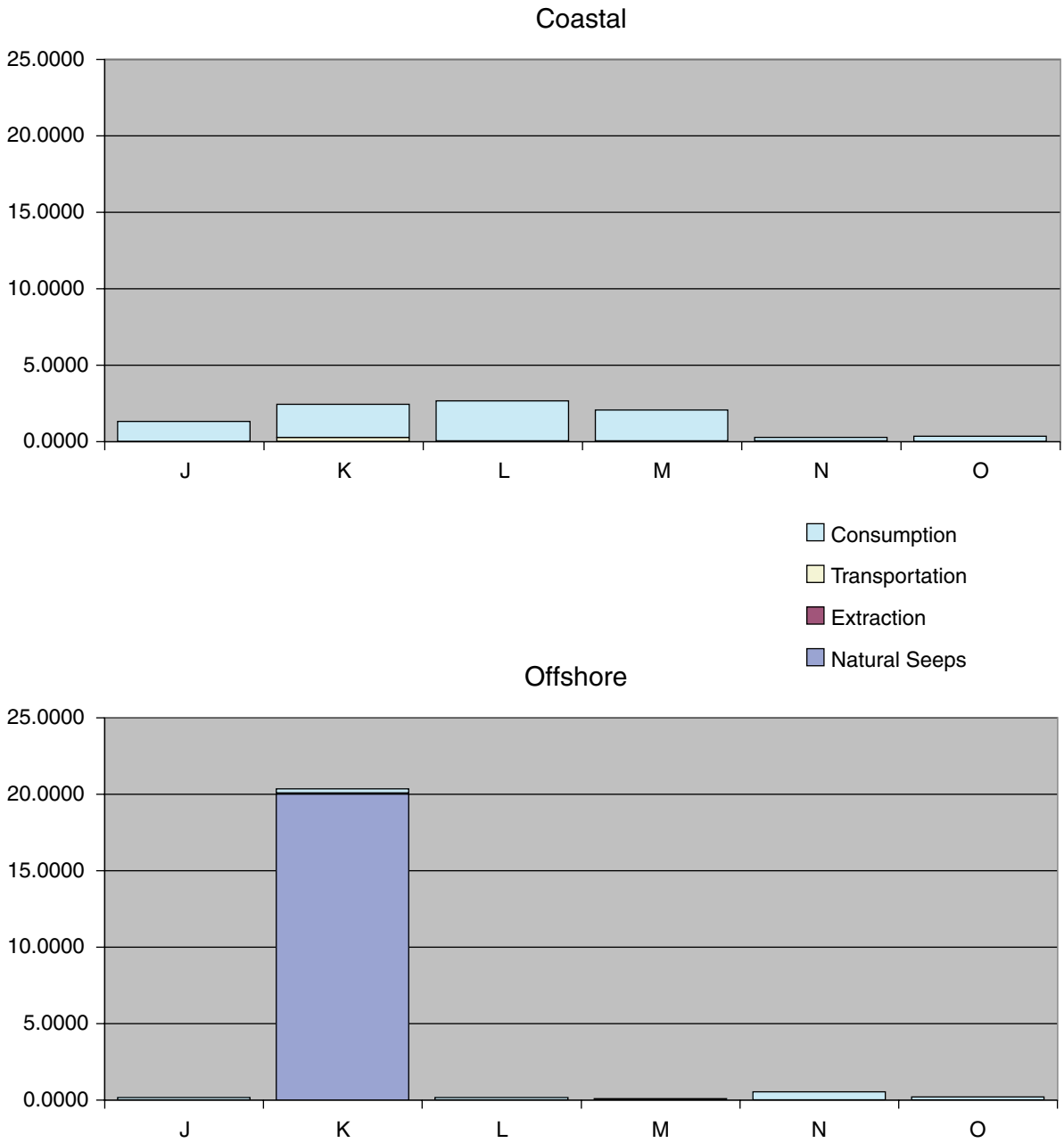

FIGURE 2-15 Average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) for the Pacific Seaboard of North America (plus Hawaii).

agencies, especially the U.S. Coast Guard, should work with the transportation industry to undertake a systematic assessment of the extent of noncompliance. If the estimates of noncompliance assumed in this report are essentially correct, more rigorous monitoring and enforcement policies should be developed and implemented.

Gasoline and lube oil inputs from two-stroke recreational vessels are a large marine source of petroleum hydrocarbons. These discharges are primarily gasoline and lube oil, which have high evaporation rates and low PAH levels. However, these inputs frequently occur near ecologically sensitive areas (estuaries, mangroves) during vulnerable stages in the life cycle of organisms. **Federal agencies, especially the EPA, should continue efforts to regulate and encourage the phase-out of inefficient two-stroke engines, and a coordinated enforcement policy should be established.**

Large quantities of VOC are discharged into the atmosphere from tank vessels and oil and gas operations. How-

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TABLE 2-9 Average Annual Input (1990-1999) of Petroleum Hydrocarbons (tonnes) for the Coastal and Territorial Waters of Alaska

ZONE (Coastal)		P	Q
Sum Seeps		**400**	**trace[a]**
	Platforms	trace	na
	Atmospheric	trace	na
	Produced	110	na
Sum Extraction		**120**	**na[b]**
	Pipelines	trace	na[c]
	Tank vessel	20	trace
	Coastal facilities	30	10
	Atmospheric	trace	trace
Sum Transportation		**60**	**20**
	Land-based	80	trace[d]
	Recreational vessels	50	20
	Vessels >100GT (spills)	70	trace
	Vessel >100GT (Op Discharge)	trace	trace
	Vessel <100GT (Op Discharge)	trace	trace
	Atmospheric	890	580
	Aircraft[e]	na	na
Sum Consumption		**110**	**600**
ZONE (Offshore)		**P**	**Q**
Sum Seeps		**na**	**na**
	Platforms	na	na
	Atmospheric	na	na
	Produced	na	na
Sum Extraction[b]		**na**	**na**
	Pipelines[c]	na	na
	Tank vessel	trace	trace
	Atmospheric	trace	trace
Sum Transportation		**trace**	**trace**
	Land-based[f]	na	na
	Recreational vessels[g]	na	na
	Vessels >100GT (spills)	30	50
	Vessel >100GT (Op Discharge)	trace	trace
	Vessel <100GT (Op Discharge)	trace	trace
	Atmospheric	210	220
	Aircraft	45	15
Sum Consumption		**290**	**300**
Grand Total		**980**	**910**
Sum of Anthropogenic		**580**	**910**

[a]Estimated loads of less than 10 tonnes per year reported as "trace"

[b]No known oil and gas production in this region (North Slope production is limited to terrestrial fields)

[c]No known coastal or offshore pipelines in this region (North Slope production is limited to terrestrial fields)

[d]Load in this region limited to petroleum hydrocarbons derived from eroded source rocks (see Chapter 3 and Appendix I)

[e]Purposeful jettisoning of fuel not allowed within 3 nmiles of land (see Chapter 3 and Appendix E)

[f]Land-based inputs are defined in this study as being limited to the coastal zone (see Chapter 3 and Appendix I)

[g]Recreational vessels are defined in this study as being limited to operations within 3 nmiles of the coast (see Chapter 3 and Appendix F)

ever, the VOC consist mostly of methane and ethane, which tend to oxidize rather than deposit in the oceans. These emissions may represent a "greenhouse gas" concern, but their atmospheric deposition into North American waters is less than 0.5 percent of all inputs, and inputs of VOC into the oceans worldwide are less than 4 percent of the estimated total. **The U.S. Coast Guard should work with the International Maritime Organization to assess the overall impact on air quality of VOC from tank vessels and establish design and/or operational standards on VOC emissions where appropriate.**

On the basis of limited data, aircraft inputs from deliberate dumping of jet fuel in the sea appear to be locally significant. **Federal agencies, especially the Federal Aeronautics Administration (FAA), should work with industry to more rigorously determine the amount of fuel dumping by aircraft and to formulate appropriate actions to limit this potential threat to the marine environment.**

Fates

The effect of petroleum hydrocarbon is not directly related to the volume released. It is instead a complex function of the rate of release, the nature of the released hydrocarbon, and the local physical and biological ecosystem. Some progress has been made in understanding the basic processes affecting fates such as evaporation. Much more needs to be learned about oil-sediment interaction, vertical dispersion and entrainment, dissolution, Langmuir cells, and hydrate formation (as related to deep subsurface releases of gas). Furthermore, the priorities for research into petroleum hydrocarbon fate and transport have historically been driven by large spills. Thus, resource allocation to support these efforts tends to wane in periods during which a large spill has not recently occurred. **Federal agencies, especially NOAA, MMS, the U.S. Coast Guard, and the USGS, should work with industry to develop and support a systematic and sustained research effort to further basic understanding of the processes that govern the fate and transport of petroleum hydrocarbons released into the marine environment from a variety of sources (not just spills).**

Response plans depend heavily on site-specific modeling predictions of the behavior of spills of various sizes and types, under a variety of environmental conditions. There is a need for both better baseline data, including ambient background levels of hydrocarbons in the sea, and better data for calibrating fate and behavior models. Because experimental release of petroleum is not feasible under most circumstances, comprehensive data on the fate of the oil must be collected during spills. Such efforts are generally neglected, because moving needed equipment and personnel to spill sites to collect data is of lower priority than containing the spill and minimizing damage to the environment and property. **Federal agencies, especially the U.S. Coast Guard,**

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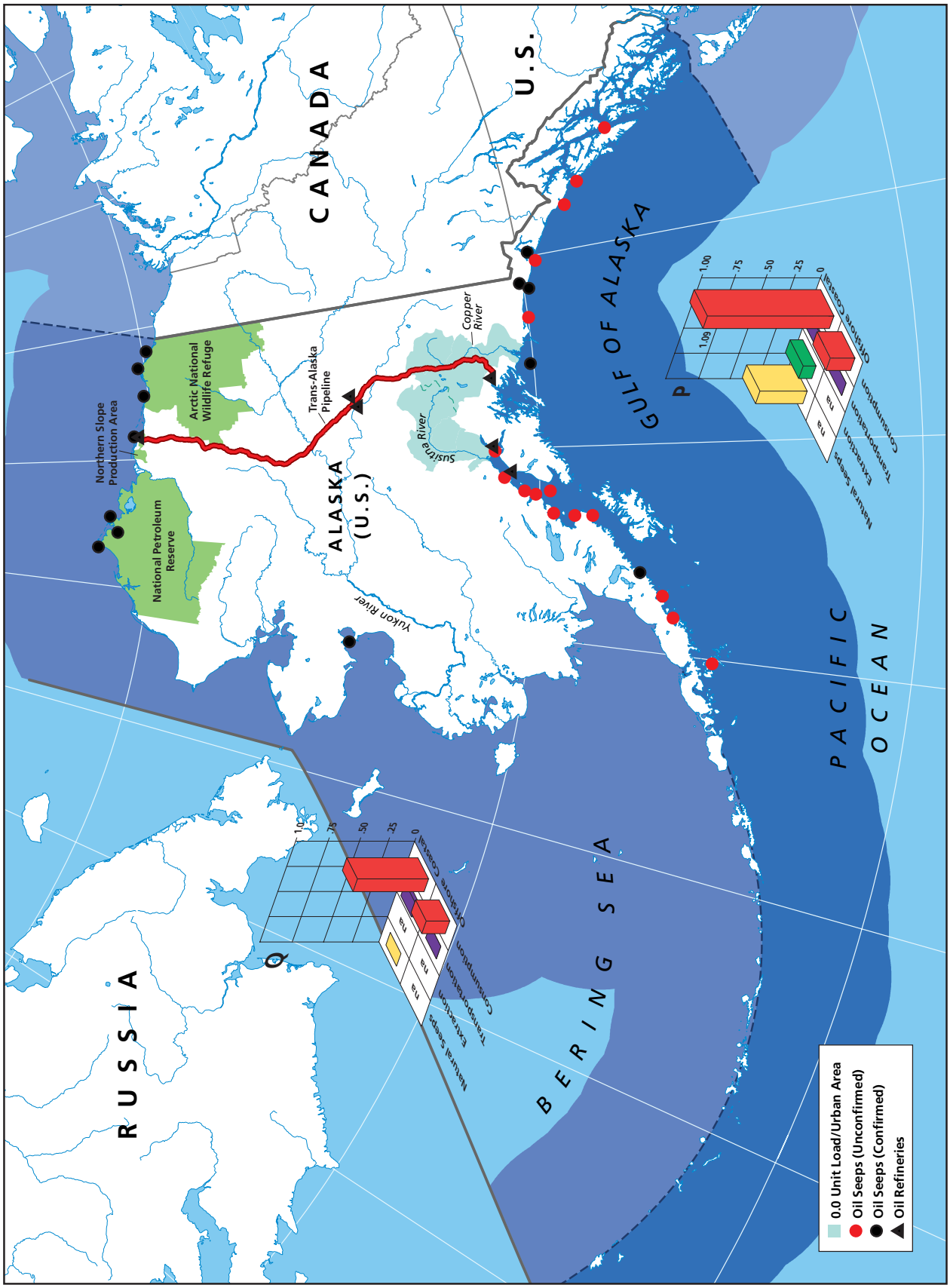

FIGURE 2-16 Average, annual input (1990-1999) of petroleum hydrocarbons (kilotonnes) for the coastal and territorial waters of Alaska. (Additional information provided by Alaska GIS Data Clearinghouse, Alaska Department of Natural Resources Division of Oil and Gas, EIA, EPA, and the U.S. Bureau of Land Management, Alaska.)

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PHOTO 5 The brightest areas of the Earth are the most urbanized, but not necessarily the most populated. (Compare western Europe with China and India.) Cities tend to grow along coastlines and transportation networks. (Image courtesy of NASA.)

NOAA, and EPA should work with industry to develop a more comprehensive database of environmental information and ambient hydrocarbon levels, and should develop and implement a rapid response system to collect in situ information about spill behavior and impacts.

Natural seep systems and sites of historical spills offer good opportunities for field studies of the fate and effect of the release of crude oil and (in the case of spills) refined products, especially to understand dissolution and long-term weathering. **Federal agencies, especially the USGS, NOAA, EPA, and MMS, should develop and support targeted research into the fate and behavior of hydrocarbons released to the environment naturally through seeps or past spills.**

Effects

Ecosystems and their components vary at time scales ranging from seasons to decades and longer. Therefore, in the absence of ongoing monitoring, it is exceedingly difficult to quantify the effects of oil in the sea, or to establish when recovery from a pollution event is complete. The establishment of monitoring programs in selected regions with an elevated risk of petroleum spills or discharges would enhance the ability to determine effects and recovery and to understand the processes controlling ecosystem responses to pollution. Existing databases on the distribution, frequency, and size of petroleum spills and existing petroleum distribution routes could be used to identify locations most appropriate for monitoring. **Federal agencies, especially the USGS and EPA, should work with state and local authorities to establish or expand efforts to monitor vulnerable components of ecosystems likely to be exposed to petroleum releases.**

The inputs and long-term fate of land-based sources (due both to runoff and to atmospheric deposition) are poorly understood. The range of uncertainty of land-based runoff of petroleum hydrocarbons is four orders of magnitude. The upper limit, if correct, would dwarf all other inputs. The loads from rivers and air inputs are not being monitored consistently, and the background inputs from rivers are virtually unknown. **To assess the impacts attributable to different sources including oil spills and non-point sources, federal agencies, especially the USGS and EPA should work with state and local authorities to undertake regular monitoring of Total Petroleum Hydrocarbon (TPH) and PAH inputs from air and water (especially rivers and harbors) to determine background concentrations.**

There are demonstrable effects of acute oiling events at both small and large spatial scales. These effects result from physical fouling of organisms and physiological responses to the toxic components of oil. Although there is now considerable information on the toxicological effects of individual components of oil, there is a lack of information about the synergistic interactions in organisms between hydrocarbons and other classes of pollutants. This problem is particu-

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larly acute in areas subject to chronic pollution, (e.g., urban runoff). Research on the cumulative effects of multiple types of hydrocarbons in combination with other types of pollutants is needed to assess toxicity and organism response under conditions experienced by organisms in polluted coastal zones. **Federal agencies, especially the USGS, MMS, NOAA, and EPA, should work with industry to develop or expand research efforts to understand the cumulative effects on marine organisms. Furthermore, such research efforts should also address the fates and effects of those fractions that are known or suspected to be toxic in geographic regions where their rate of input is high.**

There are demonstrable sublethal physiological effects of long-term, chronic releases of hydrocarbons into the marine environment. These have been found in areas affected by urban runoff, in areas where oil has been incorporated in sediments and then released back to the water column, and in production fields. Chronic sources of hydrocarbon pollution remain a concern, and their effects on populations and ecosystems require further assessment. **Federal agencies, especially the USGS, EPA, and NOAA, should work with state and local authorities and industry to implement comprehensive laboratory and field based investigations of the impact of chronic releases of petroleum hydrocarbons.**

Biogenically structured habitats, such as coastal marshes and mangrove forests, are subject to destruction or alteration by acute oiling events. Because the structure of these habitats depends on living organisms, when they are killed, the structure of the habitat, and sometimes the substrate on which it grows, is lost. Depending on the severity of oiling, and particularly if oil is incorporated in the sediments or structure of the habitat, recovery of the habitat and the organisms dependent on it may be exceptionally slow. **In areas of sensitive environments or at-risk organisms, federal, state, and local entities responsible for contingency plans should develop mechanisms for higher levels of prevention, such as avoidance, improved vessel tracking systems, escort tugs, and technology for tanker safety.**

Although there is now good evidence of the toxic effects of oil pollution on individual organisms and on the species composition of communities, there is little information on the effects of either acute or chronic oil pollution on populations or on the function of communities or ecosystems. The lack of understanding of population-level effects lies partly in the fact that the structure of populations of most marine organisms is poorly known because of the open nature of communities and the flow of recruits between regions. Also, in some populations (e.g., bony fish) the relationships between numbers of juveniles produced and recruitment to the spawning adult population are unknown. **The U.S. Departments of Interior and Commerce should identify an agency, or combination of agencies, to develop priorities for continued research on the following:**

- **the structure of populations of marine organisms and the spatial extent of the regions from which recruitment occurs;**
- **the potential for cascades of effects when local populations of organisms that are key in structuring a community are removed by oiling; and**
- **the basic population biology of marine organisms, which may lead to breakthroughs in understanding the relationship between sublethal effects, individual mortality and population consequences.**

There is a tremendous need for timely dissemination of information across state, federal, and international boundaries about the environmental effects of oil in the sea. Although the United States has experience that might benefit the international community, this nation might benefit greatly from lessons learned in other countries with offshore oil production, heavy transportation usage, and diffuse inputs of petroleum from land- and air-based sources. **Therefore, the federal agencies identified above, in collaboration with similar international institutions, should develop mechanisms to facilitate the transfer of information and experience.**

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II.

Understanding Inputs, Fates, and Effects in Detail

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3

Input of Oil to the Sea

HIGHLIGHTS

This chapter points out that:

- Chronic release from natural and anthropogenic sources (e.g., natural seeps and run-off from land-based sources) are responsible for the majority of petroleum hydrocarbon input to both North American waters and the world's oceans.
- The inputs from land-based sources are poorly understood, and therefore estimates of these inputs have a high degree of uncertainty.
- Spillage from vessels in U.S. waters during the 1990s declined significantly as compared to the prior decade, and now represents less than 2 percent of the petroleum discharges into U.S. waters.
- Operational discharges from vessels in general and tankers in particular have substantially declined over the last 25 years.
- Only 1 percent of the oil discharges in North American waters is related to the extraction of petroleum.
- Although large quantities of VOC (volatile organic compounds) are emitted from tankers and production platforms, these consist of mostly lighter compounds and only small amounts deposit to the sea surface.
- Older two-stroke engines utilized in a significant number of recreational marine vessels have high operational discharges due to inherent design inefficiencies, and are responsible for about 2 percent of the petroleum hydrocarbons introduced into North American waters each year.

Petroleum hydrocarbons enter the marine environment from numerous sources. The 1985 National Research Council report *Oil in the Sea: Inputs, Fates, and Effects* (National Research Council, 1985) was a benchmark report and basically updated the original 1975 National Research Council report *Petroleum in the Marine Environment*. Inputs from maritime transportation activities were once again updated in 1990 in a study conducted by the U.S. Coast Guard in cooperation with the National Academy of Sciences (International Maritime Organization, 1990). Increased petroleum production and consumption by industry and the public in the past 15 years warrants an updated analysis of the quantity and varied inputs of petroleum hydrocarbons into the marine environment.

Significant differences in a variety of conditions exist between those in 1985 and the present. The major differences include:

Petroleum production. In 1970, the world oil production was 7.0 million tonnes per day and by 1985, it had increased to 8.5 million tonnes per day (www.eia.doe.gov, 2001). By the end of 2000 the production had increased to 11.0 million tonnes per day, an increase of about 30 percent over the 16 years. The average annual rate of growth in production has been approximately 1.6 percent and a rate of growth of 1.9 percent has been forecast for the first decade of the 21st century. In 1985, there were only a few thousand offshore oil and gas platforms and by 1999 there were about 8,300 fixed/floating offshore platforms (DeLuca and LeBlanc, 1997). Worldwide offshore production has grown by 45 percent from 1985 to 1995, the latest year of record (API, 2001).

Volume of petroleum products transported. Since 1985, significantly higher volumes of petroleum hydrocarbons are being transported by various methods on the world's oceans.

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For example, exports to the U.S. from the Middle East grew by nearly a factor of three to 346,900 tonnes/day in 1999. For the world as a whole, the growth in exports from the Middle East increased by a factor of two (API, 2001).

Databases. Since the NRC 1985 report, significant new databases that contain more accurate information have been generated by public, governmental, and private agencies. These databases have become much more accessible with the advent of the worldwide web. In the present report, data bases existed that allowed a) dividing oil and gas operations into four categories (platforms, outer continental shelf (OCS) pipelines, coastal pipelines, and produced waters), b) estimating atmospheric deposition of petroleum hydrocarbons, and c) estimating recreational/small craft inputs. In general, the international databases for spills are neither as comprehensive nor as carefully maintained as those for U.S. and Canadian waters, and therefore the worldwide estimates have a greater uncertainty.

Regulations. Since 1981, a number of regulations intended to reduce petroleum hydrocarbon inputs into the oceans have been implemented. The 1978 Protocol of the International Convention for the Prevention of Pollution from Ships (MARPOL 73/78) was implemented in the U.S. in June 1981, and went into effect worldwide in 1983. These regulations mandate segregated ballast tanks (SBT) for new tankers and set limits on the oil content of overboard discharges. The Oil Pollution Act of 1990 (OPA 90; Appendix K) and the 1992 amendments to MARPOL 73/78 mandate double-hull requirements or equivalent protection for all new tankers, and establish phase-out schedules for existing single-hull tankers. Other relevant regulations include restrictions on produced water discharges into coastal waters of the United States, the elimination of oil-based drilling cutting into the North Sea, and limits on the average oil and grease content of produced water discharge. These and other regulatory changes have contributed to a significant reduction in both operational discharges and accidental spills.

Identification of geographic distribution of inputs. In 1985, data did not exist to accurately pinpoint the geographic area of the major sources of input of hydrocarbons to the oceans. Since then, new reporting databases contain the location of major spills, and it is now possible to subdivide the input of hydrocarbons to relatively small geographic zones in North American waters. Although similar databases exist for only a few other worldwide areas, they are still not refined enough to allow specific allocation of inputs by geographic zones.

Increase in urban population. In the fifteen years since the last NRC report, there has been a significant increase in urban population, particularly in the coastal zone. Current trends indicate that by the year 2010, 60 percent of the U.S. population will live along the coast. This is consistent with the worldwide profile in which two-thirds of the urban centers, defined as cities with populations of 2.5 million or more, are near tidal estuaries. This increased population has resulted in a considerable increase in land-based runoff of petroleum hydrocarbons.

Increase in number of two- and four-stroke engines. In 1985, the NRC report *Oil in the Sea* did not discuss petroleum hydrocarbon inputs from operation of recreational marine vehicles. In 1990, heightened awareness about the large number and design inefficiencies of these engines led the US EPA to begin regulating the "non-road engine" population under the authority of the Clean Air Act. The average hours of use nationwide for two-stroke personal watercraft engines is 77.3 hours per year and for outboard engines is 34.8 hours per year (EPA, in preparation). This increased use of two-stroke engines has proven to be a major contribution to discharge of petroleum hydrocarbons to marine waters, especially in coastal waters from recreational marine vehicles.

In the 1985 NRC report, inputs were categorized into five major sources: Natural, Offshore Production, Transportation, Atmospheric, and Municipal and Industrial. Subcategories were delineated within several of these major input areas (Table 3.1). In the present report, inputs were organized into four major sources, with subcategories within each of the major sources (Table 3-1).

Although the categories are organized slightly differently in the two reports, the major input sources are the same. In

TABLE 3-1 Input Sources in 1985 and Present Report

1985 Report	Present Report
Natural Sources	Natural seeps
Marine seeps	Extraction of Petroleum
Sediment erosion	Platforms
Offshore production	Atmospheric deposition
Transportation	Produced waters
Tanker operations	Transportation of Petroleum
Dry-docking	Pipeline spills
Marine terminals	Spills (tank vessels)
Bilge and fuel oils	Operational discharges (cargo oil)
Tanker accidents	Coastal facility spills
Non-tanker accidents	Atmospheric deposition (tanker VOC)
Atmosphere	Consumption of Petroleum
Municipal & Industrial wastes	Land-based (river and runoff)
Municipal wastes	Recreational vessel discharge
Refineries	Spills (commercial vessels ≥100 GT)
Non-refining industrial wastes	Operational discharges (vessels ≥100 GT)
Urban runoff	Operational discharges (vessels <100 GT)
River runoff	Atmospheric deposition
Ocean dumping	Aircraft dumping

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the present report, databases existed that allowed a) breaking oil and gas operations into three categories (platforms, pipelines, and produced waters), and b) separating out various types of recreational/small craft inputs (see Table 2-3 for more complete discussion of the intercomparibility of the two reports and the significance of any changes in the estimates for the various categories of input). Three known sources of petroleum, erosion of petroleum-bearing sediment, offshore disposal of urban wastewater or sewer sludge, and abandoned vessels (shipwrecks still containing petroleum or refined products) were not directly included in calculations for North America of the world. All three of these sources may be locally significantly, however, when compared to volumes generated from the more commonly recognized sources; their significance at worldwide, continental, and even regional scales is minimal. Of the three, it was felt that greater attention should be paid to potential risks posed by abandoned vessels. The vast majority of these are sunken World War II vessels, and corrosion and other factors working over the last 60 years may pose risk to increased leakage rates or catastrophic failure of the structure and sudden release of large volumes of refined product. An in-depth examination of this issue was beyond the scope and resources of the study, but greater attention may need to be paid to this potential source in the near future (Box 3-1).

PETROLEUM HYDROCARBON INPUTS

Petroleum hydrocarbon inputs into North American and worldwide marine waters were computed, based on various databases, for four major categories. These include a) natural seeps, b) extraction of petroleum, c) transportation of petroleum, and d) consumption of petroleum. Details of the methodology utilized, and discussion of the computation and distribution of sources are discussed in Appendixes C through I, the databases are explained in Appendix D. In order to further pinpoint the source of these discharges, North American waters were divided into 17 zones (Figure 2-3; see Appendix B for description). Table 3-2 summarizes the sources of inputs for North American and worldwide waters.

NATURAL SEEPS

Crude oil that seeps naturally into the marine environment establishes a contaminant "background" that needs to be measured in order to determine the extent of pollution resulting from human activities, such as oil spills. This new assessment places the current global rate of natural seepage of crude oil at 600,000 tonnes per year, with a range of 200,000 to 2,000,000 tonnes per year. These estimates take into account two previous studies of the National Research

BOX 3-1

Grounded and Abandoned Vessels

Grounded and abandoned vessels pose a significant threat of oil spills, and releases of other pollutants by becoming sites for illegal dumping of waste oils and hazardous materials. This may impede navigation, and could result in physical crushing and smothering of habitats, leading to wildlife entrapments and public health hazards. There are two different types of abandoned vessels that pose the greatest oil pollution risks:

- Derelict vessels—These vessels are generally unseaworthy or are no longer useful and have been tied up and abandoned. Others are mothballed, are awaiting repair or dismantling, or are intentionally grounded as a result of illegal activities (drug smuggling or illegal immigrants). After their moorings fail, many vessels sink, become semi-submerged in the intertidal, or strand on shorelines. These vessels typically lack insurance, have little value, and have insolvent owners. Thus, these abandoned vessels become potential sources of oil pollution, from either chronic leaks or a large release once oil storage areas fail.
- Historic wrecks—From an oil pollution perspective, wrecks sunken during and since World War II pose the greatest risks because of the presence of residual fuels. Many of these vessels are considered submerged cultural resources and some may be memorials or national historic landmarks, such as the *USS Arizona* in Pearl Harbor. Many military wrecks are war graves, and U.S. Navy policy is that the remains of crew members should remain undisturbed unless proper retrieval and burial become necessary. Therefore, oil removal and salvage actions would have to deal with the issue of disturbance of human remains. World War II wrecks are of particular concern because they can contain large volumes of oil, and corrosion after nearly 60 years underwater can lead to chronic leaks and the potential for catastrophic releases. For example, the *USS Mississinewa* (Fig. 3-1), an oil tanker sunken in 1944 in Ulithi Lagoon and containing an estimated 1-3 million gallons of a heavy fuel oil started leaking in August 2001, a few months after a storm passed over the site.

Existing U.S. and international laws and regulations provide limited authority to promptly remove grounded or abandoned vessels that are causing harm to natural resources but which are not otherwise obstructing or threatening to obstruct navigation, or threatening a pollution discharge. With the exception of the Oil Pollution Act (OPA), no federal statute provides a source of funds other than appropriated agency monies for use in removing grounded or abandoned vessels, and the OPA fund has not been made broadly available for these purposes.

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FIGURE 3-1 The sinking of the tanker *U.S.S. Mississinewa* AO-59, Ulithi Lagoon, November 20, 1944. (Photo courtesy of Simon Harris.)

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TABLE 3-2 Average, Annual Releases (1990-1999) of Petroleum by Source (in thousands of tonnes)

	North America				Worldwide		
	Best Est.	Regions[a]	Min.	Max.	Best Est.	Min.	Max.
Natural Seeps	160	160	80	240	600	200	2000
Extraction of Petroleum	3.0	3.0	2.3	4.3	38	20	62
Platforms	0.16	0.15	0.15	0.18	0.86	0.29	1.4
Atmospheric deposition	0.12	0.12	0.07	0.45	1.3	0.38	2.6
Produced waters	2.7	2.7	2.1	3.7	36	19	58
Transportation of Petroleum	9.1	7.4	7.4	11	150	120	260
Pipeline spills	1.9	1.7	1.7	2.1	12	6.1	37
Tank vessel spills	5.3	4.0	4.0	6.4	100	93	130
Operational discharges (cargo washings)	na[b]	na	na	na	36	18	72
Coastal Facility Spills	1.9	1.7	1.7	2.2	4.9	2.4	15
Atmospheric deposition	0.01	0.01	trace[c]	0.02	0.4	0.2	1
Consumption of Petroleum	84	83	19	2000	480	130	6000
Land-based (river and runoff)	54	54	2.6	1900	140	6.8	5000
Recreational marine vessel	5.6	5.6	2.2	9	nd[d]	nd	nd
Spills (non-tank vessels)	1.2	0.91	1.1	1.4	7.1	6.5	8.8
Operational discharges (vessels ≥100 GT)	0.10	0.10	0.03	0.30	270	90	810
Operational discharges (vessels<100 GT)	0.12	0.12	0.03	0.30	nd[e]	nd	nd
Atmospheric deposition	21	21	9.1	81	52	23	200
Jettisoned aircraft fuel	1.5	1.5	1.0	4.4	7.5	5.0	22
Total	260	250	110	2300	1300	470	8300

[a]"Regions" refers to 17 zones or regions of North American waters for which estimates were prepared.
[b]Cargo washing is not allowed in U.S. waters, but is not restricted in international waters. Thus, it was assumed that this practice does not occur frequently in U.S. waters (see Chapter 3 and Appendix E).
[c]Estimated loads of less than 10 tonnes per year reported as "trace"
[d]World-wide populations of recreational vessels were not available (see Chapter 3 and Appendix F).
[e]Insufficient data were available to develop estimates for this class of vessels (see Chapter 3 and Appendix E).

NOTES:
1. Totals may not equal sum of components due to independent rounding.
2. Generally assumes an average specific volume of oil at 294 gallons per tonne (7 barrels per tonne). Where the specific commodity is known, the following values are applied when converting from volume to weight:
Gasoline: 333 gallons per tonne
Light Distillate: 285 gallons per tonne
Heavy Distillate: 256 gallons per tonne
Crude Oil: 272 gallons per tonne
3. Numbers reported to no more than 2 significant figures using rules:
http://web.mit.edu/10.001/Web/Course_Notes/Statistics_Notes/Significant_Figures.html#Significant Figures

Council (NRC, 1975; NRC, 1985) and new information on the natural seepage of crude oil into the marine environment (detailed in Appendix C). Not considered in the new or previous studies is the contribution to the marine environment of hydrothermally-derived petroleum at oceanic spreading axes (see summary by Kvenvolden and Simoneit, 1990). Although it is clear that hydrothermal petroleum occurs in the sea, the rates of seepage are unknown, but are believed to be very small, and therefore are not included in the new global assessment.

In 1975, the estimated worldwide rate of natural seepage of oil into the marine environment ranged widely from 200,000 to 6,000,000 tonnes per year, with a "best estimate" of 600,000 tonnes per year. These rates were based on a comprehensive global survey incorporating extensive geological considerations, but used extrapolations from only a few known seeps. In 1985, little new information had become available, and estimates of individual oil-seep rates had not changed significantly. Thus a revised estimate of the global seepage rate was calculated based on assumptions concerning the amount of crude oil known to be present that could seep over reasonable periods of geologic time. This theoretical approach was first developed by Kvenvolden and Harbaugh (1983) and incorporated into NRC (1985). The

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new estimates ranged between 200,000 and 2,000,000 tonnes per year, with a "best estimate" of 600,000 tonnes per year. This revised estimate does not imply that seep rates decreased during the intervening years between 1975 and 1985, but rather reflect a difference in approaches to making the global estimates.

Although only a few new seeps have been identified and estimates of known crude-oil deposits throughout the world have not changed greatly from about 300,000 million tonnes, new technologies, particularly remote sensing techniques, have provided better means of natural seep detection and assessment. Studies in parts of the Gulf of Mexico (MacDonald et al., 1993; MacDonald, 1998; Mitchell et al., 1999), using these new technologies, have resulted in an estimated seepage rate for the entire Gulf of Mexico of 140,000 tonnes per year (range of 80,000 to 200,000 tonnes per year). For offshore southern California, a new estimate of rate of oil seepage is 20,000 tonnes per year (range of 2,000 to 35,000 tonnes per year), based on considerations of work by Fischer (1978), Clester et al. (1996), and Hornafius et al. (1999). The rate of oil seepage for offshore Alaska is also estimated, based mainly on a report by Becker and Manen (1988), to be about 400 tonnes per year (range of 200 to 800 tonnes per year). The North American best estimate is 160,000 tonnes per year, with a minimum of 80,000 tonnes per year (50 percent of best estimate), and a maximum of 240,000 tonnes per year (best estimate + 50 percent[1]).

The new North American estimate of 160,000 tonnes per year is only 40,000 tonnes less than the 1985 global estimate of 200,000 tonnes per year, suggesting that the 1985 value was grossly underestimated. To accommodate the new information now available, the "best estimate" of the global crude oil seepage rate has been revised to 600,000 tonnes per year, reviving an estimate made originally in 1975. The estimated range of 200,000 tonnes per year to 2,000,000 tonnes per year was developed based on the approach applied in NRC (1985). These limits are set by the amount of crude oil seepage estimated for North American waters and the amount of crude oil ultimately available for natural seepage during geologic time.

Extraction of Petroleum

Global production of petroleum (crude oil and natural gas plant liquids) increased by 1.0 million tonnes per day (7.1 million barrels per day) between 1990 and 1999, an average annual rate of growth of 1.0 percent (International Energy Review, 1999; www.eia.doe.gov). Saudi Arabia, the United States, and Russia were the three largest producers of petroleum in 1999. Together, they produced 31.4 percent of the world's petroleum. Production from Iran and Mexico accounted for an additional 9.7 percent.

Oil and gas operations include discharges from platforms and other offshore facilities in both federal waters and state waters, produced waters, and atmospheric deposition from the volatile organic compounds (VOC) generated from offshore production platforms. Details concerning data sources, methodology, and computations can be found in Appendix D.

Platforms

Volumes of petroleum hydrocarbons introduced into North American waters from accidental discharge on offshore platforms are relatively well known for the U.S. Outer Continental Shelf and Canada, but data from offshore Mexico and state waters in the United States are generally lacking or scattered and incomplete. There are an estimated 4,900 platforms in North American waters. As of 1993, there were 3,182 offshore oil and gas facilities located in non-North American waters (International Association of Oil and Gas Producers, 2000). Thus in the world's oceans, slightly in excess of 8,000 platforms and offshore facilities provide the source of petroleum hydrocarbon input into marine waters.

In North American waters, the input of petroleum hydrocarbons from platforms is 146 tonnes per year. Platforms in the OCS account for 39 percent of the discharge, while platforms in state waters account for the remaining discharge (61 percent). As these data are based on relatively good data bases (Appendix D) accumulated over the past ten years, the committee's best estimate of inputs by offshore facilities is 153 tonnes per year (minimum plus 5 percent[2]). The committee estimated that the maximum input would probably be on the order of 20 percent[3] higher than the calculated amount or 175 tonnes per year. Based on the distribution of accidental spills identified in the databases, it was possible to further pinpoint geographically the sources of inputs. The central and western Gulf of Mexico accounted for roughly 90 percent of the total discharge in North American waters.

In marine waters worldwide (including North American waters), the calculated amount of discharge is 290 tonnes per year, a figure computed on the assumption that the vol-

[1]The 50 percent factor applied to develop a minimum and maximum estimate is somewhat subjective and reflects the committee's confidence in the ability to estimate area of slicks, range in slick thickness, and the likelihood that all seeps are accounted for.

[2]Roughly 5 percent of the spills reported in the available databases did not have adequate geographic information to place them in any region with confidence. The 5 percent factor applied to develop the best estimate reflects the committee's confidence in the reporting of spills, the completeness of available databases, and a recognition that 97 percent of the total spill volume captured by these databases comes from spills that exceed 100 gallons. The likelihood that a spill much larger than that will go unobserved is, in the committee's opinion, rather small.

[3]The 20 percent factor applied to develop an maximum estimate is somewhat subjective and reflects the committee's confidence in the reporting of spills, the completeness of available databases, and a recognition that 97 percent of the total spill volume captured by these databases comes from spills that exceed 100 gallons. The likelihood that a spill much larger than that will go unobserved is, in the committee's opinion, rather small.

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ume of spills/platform/year for foreign platforms is similar to those in North American waters. However, because not all foreign platforms are subject to the same stringent anti-pollution guidelines under which U.S. oil platforms operate, it is generally agreed that their spills/platform/year exceed the estimates for North American waters. The 1985 report estimated that foreign spills/platform/year exceeded those in the United States by 300 percent, or 860 tonnes/year and these figures were used in this report as well. The maximum is estimated to be 1,400 tonnes per year or five times the calculated amount. These latter two estimates (best and maximum) are based on the lack of any reliable databases of measured discharges from platforms in the world's oceans.

Atmospheric Deposition

During the production, transport, and refining of hydrocarbons, volatile compounds escape to the atmosphere. Some, like methane, are light and mix or degrade rapidly. Heavier compounds, like hexadecane, react more slowly and may deposit to the sea surface. These heavier hydrocarbons are labeled as volatile organic compounds (VOC) and are defined in the U.S. Clean Air Act to include all volatile hydrocarbons except methane, ethane, a wide range of chlorofluorocarbons (CFC), hydrochlorofluorocarbons (HCFC), and a few others, e.g., acetone. VOC from production facilities were not estimated in the 1975 or 1985 NRC reports. With the increased number of offshore oil and gas platforms, the committee decided to evaluate the existing databases, and make estimates of this input. Appendix D describes the methodology, databases, and calculations.

The methodology used was to take estimates from regulators or producers from the four regions where these were available (North Sea, Norwegian Sea, California, and Gulf of Mexico). For the other regions, an estimate was made by multiplying the regional production volume by an average VOC rate per unit produced based on the average of the rates for the four regions mentioned above. Lower (upper) bound VOC estimates were calculated using the same technique except that the minimum (maximum) VOC rate of the four regions was used.

Equilibrium calculations as described in Appendix D indicate that less than 0.2 percent of the released VOC are deposited to surface waters. Based on the best estimate of VOC emissions of 60,000 tonnes (VOC heavier than butane) to North American coastal waters from production platforms, 120 tonnes of VOC enter the coastal oceans from production platforms. The minimum is 72 tonnes or 60 percent of the best estimate, and the maximum is 450 tonnes or 375 percent of the best estimate[4]. Worldwide, the best estimate is 1,300 tonnes, the minimum estimate is 380 tonnes (29 percent of the best estimate), and the maximum estimate is 2,600 tonnes (200 percent of the best estimate). The significance of these VOC inputs to the marine environment are not known and will be explored to some degree in Chapter 5. However, the size of the loads suggest that they may have an impact on local air quality. VOC is a known pollutant and has been the subject of many NRC studies (NRC 1992, 1995, 1999a,b).

Produced Waters

During oil or gas production, water from the reservoir is also pumped to the surface. Under current industry practices, this "produced water" is treated to separate free oil and either injected back into the reservoir or discharged overboard. Produced water is the largest single wastewater stream in oil and gas production. The amount of produced water from a reservoir varies widely and increases over time as the reservoir is depleted. For example, in the North Sea, a maturing oil production area, the volume of produced water has increased at a rate of 10 to 25 percent per year over the period 1993-1997 in Norway (NOIA, 1998) and the United Kingdom (UKOOA, 1999).

Produced water discharges are permitted as operational discharges. The oil and grease content is regulated by permit, and the allowable maximum concentrations vary by region and nation. For the U.S. Gulf of Mexico offshore oil and gas industry, the limit is a monthly average of 29 mg/L (USEPA, 1996a); in the North Sea and Canada, it is 40 mg/L (PARCOM, 1986, PanCanada, 1999). Conventional treatment consists of gas flotation and/or membrane filtration to separate oil and water, and there will have to be major technological advances before significant improvements in treatment efficiencies can be expected.

In the United States, operators are required to routinely monitor the volumes and oil content of produced water discharges and to submit reports to regulatory authorities to demonstrate compliance with discharge permits. For Canada, Texas Territorial Seas, California, and Alaska, compiled data were available on the volume and oil content of produced water discharges, and the best estimates were calculated using these reported data for selected time periods (usually the late 1990s). Petroleos Mexicanos published an annual report (PEMEX, 2000) reporting a total amount of oil discharged in tonnes. For discharges to the Gulf of Mexico OCS and the Louisiana Territorial Seas, only produced water volumes were available. Therefore, a default value of 29 mg/L, which is the maximum amount allowed on a monthly basis for the Gulf of Mexico discharges, was used as the maximum amount of oil and grease in produced water for these areas. Many operators are able to achieve levels below 20 mg/L (long-term average for California was 18 mg/L and for Alaska was 15 mg/L). Thus, 20 mg/L was used to calculate the best estimate, and 15 mg/L was used to calculate the minimum estimate for this region.

[4]The 60 percent factor used to develop a best estimate and the 375 percent factor applied to develop an maximum estimate is somewhat subjective and reflects the committee's confidence in the data available and the methods and assumptions used to complete the calculation.

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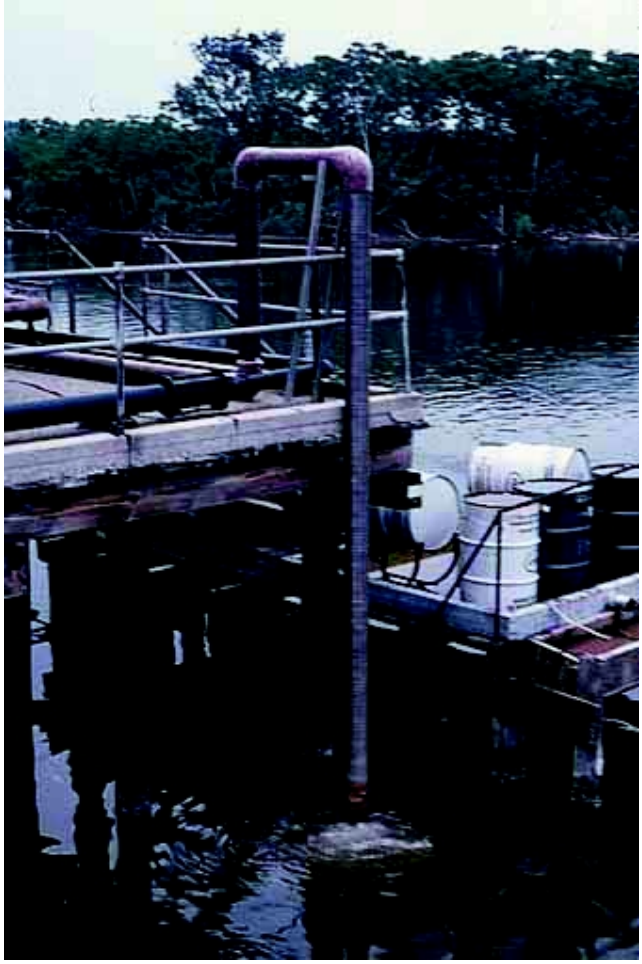

PHOTO 6 Surface water disposal of produced water discharge in estuary of south Louisiana. Water from petroleum-bearing strata (referred to as "produced water") is recovered when crude oil is pumped to the surface. Although direct disposal is no longer permitted in sensitive coastal habitats in the United States, similar practices continue in other parts of the world. (Photo courtesy of Nancy Rabalais).

The calculated minimum value of the inputs into North American waters is 2,100 tonnes per year. The best estimate is 2,700 tonnes per year and the maximum is 3,700 tonnes per year (Table D-8, Appendix D).

In the North Sea, operators sample twice each day and prepare annual summaries that report the total produced water volumes, average oil content, and total amount of oil discharged to the sea. These reports are posted on web sites by the offshore operator associations for each country. The best estimate of 8,200 tonnes of oil discharge into the North Sea was derived directly from the annual summaries by operators in the United Kingdom, Norway, The Netherlands, and Denmark (Table D-8, Appendix D). The minimum and maximum estimates for the North Sea were calculated using a low oil and grease concentration of 15 mg/L (same as for North America) and a high concentration of 40 mg/L (the maximum allowed monthly average concentration in the North Sea). The exception is Denmark, where no range estimates were made because the oil and grease content was not reported. For other international areas, where discharge summaries could not be obtained, a rough estimate was made as outlined in Appendix D.

The best estimate of the worldwide total amount of oil discharged with produced water during the late 1990s is 36,000 tonnes per year, with a minimum estimate of 19,000 tonnes per year and a maximum estimate of 58,000 tonnes per year. These volumes cannot be compared with the estimates made in the NRC 1985 report because of the different methods used to make the two estimates.

There have been some major changes in permitted discharges for the oil and gas production industry during the 1990s that are not included in Table 3-2. In the United States, produced water discharges into estuarine areas landward of the shoreline (prohibited in 1996) in Louisiana were estimated to include 1,170 tonnes per year of oil and grease (Boesch and Rabalais, 1989b). Before the prohibition of discharge of drilling muds in 1997, oil discharges with drilling cuttings were about 4,000 tonnes/year and accounted for 40 percent of the total oil releases to the North Sea by the United Kingdom.

Overall

In the NRC 1985 report, the best estimate of petroleum hydrocarbons into the world's oceans from oil and gas operations was 50,000 tonnes per year, with minimum and maximum of 40,000 and 60,000 tonnes per year, respectively. The estimates computed in this report for inputs during extraction processes are lower than the 1985 estimates, with the best estimate being 38,000 tonnes per year, with a minimum of 20,000 tonnes per year and a maximum of 62,000 tonnes per year. The concern of offshore safety and environmental compliance, differences in computing techniques, and the existence of better databases are probably responsible for the differences. In North American waters, the best estimate of petroleum hydrocarbons discharged during extraction processes is 3,000 tonnes per year, while the minimum is 2,300 tonnes per year and the maximum is 4,300 tonnes per year.

Transportation of Petroleum

Significant petroleum hydrocarbon inputs into the oceans from petroleum transportation activities include oil spills and operational discharges from tankers and pipelines, atmospheric deposition of volatile organic compounds (VOC) vented from tankers, and coastal facility spills. Details concerning data sources, methodology, and computations can be found in Appendix E.

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Pipelines

Minerals Management Service indicates that there are 21,000 miles of pipelines in U.S. Outer Continental Shelf area (www.mms.gov/stats/), and DeLuca and LeBlanc (1997) estimate that there are 23,236 miles of offshore pipelines in North America. This represents a significant increase in petroleum hydrocarbons being transported during the past decade. In OCS waters, some 75 accidental spills occurred from 1990 to 1999, discharging a total 5,674 tonnes of petroleum hydrocarbons in the marine environment (Box 3-2). Based on the databases from Minerals Management Service on OCS spills and databases from coastal waters, the average annual discharge is calculated as 1,700 tonnes per year. Even though the database is fairly complete, there is always the uncertainty of estimating the volume of the discharges. The committee's best estimate is 1,900 tonnes per year (minimum + 10 percent) with a maximum value of 2,100 tonnes per year (minimum +20 percent).[5] An estimated 99 percent of the pipeline spills occurred in the central and western Gulf of Mexico, 66 percent (1,200 tonnes per year) of the spills occurred in state waters, while 34 percent (650 tonnes per year) occurred in OCS waters.

Estimating the volumes of discharge from pipelines worldwide is more difficult and uncertain. The number of miles of offshore pipelines in the world's oceans (including North America OCS waters) has been estimated to be 82,748 miles (DeLuca and LeBlanc, 1997). This estimate is prob-

[5]The 10 percent factor used to develop a best estimate and the 20 percent factor applied to develop an maximum estimate is somewhat subjective and reflects the committee's confidence in the reporting of spills, the completeness of available databases, and a recognition that 97 percent of the total spill volume captured by these databases comes from spills that exceed 100 gallons. The likelihood that a spill much larger than that will go unobserved is, in the committee's opinion, rather small.

BOX 3-2

Lake Barre Pipeline Break, Louisiana

In May 1997 an underwater pipeline rupture released 940 tonnes (280,000 gallons) of south Louisiana crude oil into Lake Barre, Louisiana. Lake Barre is part of a shallow coastal estuarine system separated from the Gulf of Mexico by barrier islands. Rates of subsidence in this area are among the highest in Louisiana, which among other factors results in extensive erosion of the marsh and creation of a very complex shoreline with isolated patches of sparse salt marsh and large expanses of open water. There had been such rapid change that aerial photographs taken in 1995 (two years before) were useless as base maps, and new aerial photographs had to be obtained. Water depth is about 2 m, and the tidal range is less than 1 m, and water-level changes are mostly wind-driven.

South Louisiana crude is a medium crude oil (API gravity of 31), and approximately 36 percent of the oil was estimated to have evaporated or dispersed within 48 hours. Steady onshore winds during the spill raised water levels in the marsh, and oil slicks and sheens eventually spread over 1,750 hectares (4,327 acres) of wetlands (Lorentz et al., 2001). With the high water levels and the sparse vegetation in the marsh, pockets of heavy oil trapped along the outer marsh fringe generated silver to rainbow sheens that dispersed north (downwind) through the marsh for over 6.5 km. Because of the high water levels, there was very little sediment contamination, and only 0.1 hectares (0.3 acres) of salt marsh died back. The oil left a black band a few tens of centimeters high on the vegetation on about 65 hectares (162 acres) of marsh. The widely spread sheens affected 1,685 hectares (4,165 acres) of wetlands over a two week period; two months later there was no evidence of oil or oil effects in these lightly oiled areas. Response efforts focused on recovery of floating black oil pooled in the edges of the marsh. Of greatest concern was that cleanup should not cause more damage to the vegetation, thus a rule was instituted, and strictly enforced, that responders were to remain in boats while working in the marsh.

Water samples collected five days after the release contained 0.6-2.2 ppb total PAH, dominated by naphthalenes. Limited sediment sampling indicated no large-scale contamination of bottom sediments. Residual petroleum hydrocarbons in sediment samples collected one year later were characterized as significantly weathered, with degradation of nearly all *n*-alkanes.

The only reports of dead fish or shellfish were three dead juvenile blue crabs (although adult crabs and fish were alive) in a total of seven crab pots inspected, some dead brown shrimp in a survey trawl, and a few dead forage fish in the marsh. An oil fates and effects model was used to estimate that 7,500 kg of fish and invertebrates were lost (Kern et al., 2001).

Estimating impacts to birds was difficult because the summer residents are mostly rails, small shorebirds, and similar birds that hide in marsh grass. Only two birds were found oiled and dead; 58 live oiled birds were observed but not captured. The bird impacts would have been significantly different if the spill had occurred in winter when very large numbers of wintering waterfowl are present.

Key factors that limited the biological impacts of this spill were: a crude oil that was highly degradable; rapid weathering of the oil because it spread over a large surface area; calm sea conditions so there was little mixing of oil into the water column or contamination of bottom sediments; time of year when relatively few birds were present; and little intertidal sediments so the oil did not strand onto the marsh substrate.

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PHOTO 7 Crude oil is heated to maintain low viscosities, thereby making pipeline transport from offshore easier. Low temperatures can also lead to the formation of gas hydrates in pipelines crossing the sea bed. (Photo courtesy of Environmental Research Consulting.)

ably too low by as much as 30 percent, but these are the only published figures available.

The computed minimum volume spilled is 6,100 tonnes/year and is based on the volume of petroleum hydrocarbons spilled per mile of pipeline per year in North American waters. Because of the uncertainty of the number of miles of pipelines existing in non-North American waters and the lack of adequate databases, the best estimate is 12,000 tonnes per year or two times the calculated amount, while the maximum spillage is estimated to be 37,000 tonnes per year or six times the calculated amount.

Spills (Tank Vessels)

During the period from 1980 to 1999, the size of the tanker fleet has been relatively stable, with the number of

PHOTO 8 Even a relatively small spill (one gallon) can generate a visible slick that extends for some distance from the source. Additional research is needed to evaluate the cumulative impact of such small releases that occur regularly in a given area, especially when they occur in sensitive areas such as coastal wetlands. (Photo courtesy of Nancy Rabalais.)

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tankers increasing from 7,112 to 7,270, and the deadweight of the tanker fleet decreasing from 340 million tonnes to 299 million tonnes. Due to the phase-out schedule of OPA 90 and MARPOL Regulation 13G, the fleet is becoming younger, such that in 1999 more than 50 percent of the tanker fleet was less than 15 years of age. In recognition of the fundamental changes that took place after the *Exxon Valdez* accident, spill data from 1990 onward were used as the basis for estimating the amount of oil spilled from tankers (tank ships and tank barges). The U.S. Coast Guard consistently collected data on oil spills during the 1990s. These data are considered reliable, particularly for the larger spills, and they serve as the basis for the estimated spills in U.S. waters. The data were sorted geographically to remove inland spills. During the period from 1990 to 1999, there were 513 spills from tankers and tank barges in U.S. coastal waters of at least 100 gallons in size, and the average annual spillage was 4,000 tonnes. Of the recorded spills, 64 were greater than 10,000 gallons (34 tonnes) in size, and these accounted for over 95 percent of the total spillage. One single spill of 13,000 tonnes (3.9 million gallons) from the *Mega Borg* in 1990 accounted for 36 percent of the total spillage during this ten-year period.

Because comprehensive spill databases for Canadian and Mexican waters are not available, spill volumes for these waters were estimated by adjusting the U.S. figures by the relative movements of petroleum. On this basis, the calculated oil spillage to North American waters, from tankers is 4,000 tonnes per year (see Table 3-2). This calculated value was taken as the minimum estimate. Recognizing the completeness of the U.S. data set, the spill quantities were increased by 5 percent to 5,300 tonnes to obtain the best estimate, and by 20 percent to 6,400 tonnes to obtain the maximum estimate.[6]

International spill data were obtained from the *Environmental Research Consulting* database and includes information gleaned from the International Maritime Organization, ITOPF, and other national and regional agencies. These international data are not consistently collected and do not include spills under 10,000 gallons (34 tonnes) in size, and are therefore regarded as underestimates. The international spill quantities were increased by 25 percent to obtain the minimum estimate, by an additional 10 percent to obtain the best estimate, and further increased by 25 percent to obtain the maximum estimate. The international and North American figures were then combined to produce the worldwide estimates of spillage from tankers. The best estimate is 100,000 tonnes; the minimum and maximum estimates are 93,000 tonnes and 130,000 tonnes, respectively.

The NRC 1985 report and the 1990 study (IMO, 1990) both used data from the International Tanker Owners Pollution Federation Ltd. (ITOPF) to estimate the quantity of oil entering the marine environment from tanker accidents. In the NRC 1985 report, the spillage from tankers was averaged over the 7-year period from 1974 to 1980, establishing a best estimate of 390,000 tonnes per year. In the 1990 study, the spillage from tankers was averaged for the 10-year period from 1981 to 1989, establishing a best estimate of 114,000 tonnes per year. It is believed that the collection of international data prior to 1990 was even less consistent than it is today. Also, in the 1985 and 1990 reports no adjustments were made for the deficiencies in the database, and therefore care should be taken when comparing these estimates. In U.S. waters where the spill data have been more consistently recorded since 1980, spillage from tankers during the period 1990-1999 was less than one-third of the spillage recorded during the period 1980-1989.

Operational Discharges (Cargo Oil)

During normal operations, certain tankers may discharge into the sea an amount of oil contained in the ballast and tank washings. Under regulation 13 of MARPOL 73/78, tankers of 20,000 tonnes deadweight and above are required to have segregated ballast tanks (SBT), dedicated clean ballast tanks (CBT), and/or crude oil washing systems (COW), depending on the vessel type, when they were built, and their size. Regulation 13F adopted in 1992 requires all new tankers to have double-hull or equivalent protection of all oil tanks within the cargo block. MARPOL Regulation 13G requires mandatory retirement for single hull tankers at 30 years of age. A revision to regulation 13G requires phase-out of all single hull tankers above 20,000 tonnes deadweight by 1 January 2007.

Generally, crude oil carriers of 20,000 deadweight tonnes (DWT) and above and product tankers of 30,000 tonnes deadweight and above delivered since 1983 must have SBT. Segregated ballast tanks are ballast tanks that are completely separated from the cargo oil and fuel oil systems, and are permanently allocated to the carriage of water ballast. SBT greatly reduces the likelihood of oily ballast discharge, because there are sufficient segregated ballast tanks for normal operation in ballast. For these vessels, ballast may be allocated to cargo tanks only when needed to ensure the safety of the vessel in particularly severe weather. Unlike SBT, the piping systems for CBT may be common or connected with the cargo oil pump and piping systems. There are few CBT tankers operating today.

Regulation 9 of MARPOL limits the amount of oil that may be discharged into the sea to 1/15,000 of the total cargo oil volume for tankers built prior to the implementation of

[6]Roughly 5 percent of the spills reported in the available databases did not have adequate geographic information to place them in any region with confidence. The 5 percent factor applied to develop the best estimate reflects the committee's confidence in the reporting of spills, the completeness of available databases, and a recognition that 97 percent of the total spill volume captured by these databases comes from spills that exceed 100 gallons. The likelihood that a spill much larger than that will go unobserved is, in the committee's opinion, rather small.

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MARPOL73 (commonly referred to as Pre-MARPOL tankers), and 1/30,000 of the total cargo oil volume for MARPOL tankers. The requirement that the oil content of discharged effluent cannot exceed 15 ppm has the practical effect of limiting operational discharge to amounts much less than these maximum values.

Discharge of oily water within 50 nautical miles from shore is prohibited. Therefore, operational discharges from tankers in North American waters were presumed to be zero. Intentional discharges within U.S. and Canadian waters are believed to be small due to rigorous enforcement programs, and such intentional discharges are considered as part of the input from spills.

By 1999, approximately two-thirds of the tankers operating worldwide had either SBT or double-hull arrangements. SBT and double-hull crude oil carriers will water wash 3 to 4 cargo tanks twice a year for inspection purposes. Assuming full compliance with MARPOL and an oil content of 15 ppm for the discharged effluent, the total discharge per year from SBT and double-hull tankers is estimated as 95 tonnes per year.

The remaining one-third of the crude oil carriers are Pre-MARPOL vessels, and they carry ballast in their cargo tanks. For MARPOL compliant operations, the committee estimated that 1/200,000 of the cargo oil moved on these Pre-MARPOL vessels is discharged with the ballast. This assumes that 30 percent of the deadweight is discharged as ballast with an oil content of 15 ppm. If all Pre-MARPOL tankers operate in compliance with MARPOL, the total estimated discharge is 5,000 tonnes per year.

The outflow factor (oil discharge expressed as a fraction of the oil moved) is estimated as 1/2,000,000 for SBT and double-hull product tankers, and 1/200,000 for Pre-MARPOL product tankers. Assuming all vessels are MARPOL compliant, the estimated operational discharge is 380 tonnes per year for SBT and double hull product tankers, and 1,900 tonnes per year for non-SBT product tankers.

Thus, if all tankers operate in strict compliance with MARPOL, the total operational discharge from cargo washings and ballast discharge is estimated to be 7,400 tonnes per year. It is recognized that not all vessels comply with the regulatory requirements, and the following levels of compliance were assumed when calculating worldwide operational discharges:

Greater than 125,000 DWT	99 percent compliance
20,000 to 125,000 DWT	95 percent compliance
Less than 20,000 DWT	90 percent compliance

The rationale for this degree of non-compliance is that: 1) not all tankers fly the flag of a State that is party to MARPOL 73/78; 2) not all tankers that fly the flag of a State party to MARPOL 73/78 operate in compliance with the discharge criteria; 3) there will be equipment failures on board ships; and 4) there are not adequate reception facilities worldwide. The higher degree of compliance allocated to the larger tankers was justified on the basis that the majority of the larger tankers fly the flag of a State party to MARPOL 73/78, and the majority of larger tankers are on longer voyages that facilitates compliance with MARPOL 73/78.

When these levels of compliance were factored into the analysis, the best estimate for total operational cargo oil discharge from tankers was calculated to be 36,000 tonnes per year. Due to the uncertainty in estimating the frequency of non-compliance and the expected discharge in the event of non-compliance, the minimum estimate is 18,000 tonnes (one-third of the best estimate), and the maximum estimate is 72,000 tonnes (twice the best estimate).[7]

In the 1975 NRC, 1985 NRC, and 1990 IMO reports, the best estimates for operational discharges from tankers were 1,080,000 tonnes/year, 710,000 tonnes/year, and 158,600 tonnes per year, respectively. The new estimate of 36,000 tonnes/year follows this trend of reduced operational discharges from tankers. Further reductions are anticipated in future years when the tanker fleet is fully double-hulled.

Atmospheric Deposition (from Tankers)

Tankers emit volatile organic compounds (VOC) during loading, during crude oil washing operations, and during the course of the voyage. The amount of VOC emissions depends on many factors, including the properties of the cargo oil, the degree of mixing and temperature variations experienced during the voyage, and whether a vapor recovery system is employed during loading operations. Precise measurement of VOC loss from tankers is difficult. Cargo insurance companies will typically exclude coverage for loss of 0.5 percent of a crude oil cargo as normal variation between loading and unloading ports. This is the upper range of potential uncovered loss.

INTERTANKO conducted an extensive research program to investigate the behavior of crude oil during transport (INTERTANKO, 2000). About 2,024 crude oil and VOC samples were taken during a total of 361 voyages. On the basis of CRUCOGSA study and further theoretical analysis, INTERTANKO estimates that total VOC emissions is approximately 0.20 percent of the crude oil movements, roughly half of these emissions occurring during transport and half during the loading process. In an information paper submitted to IMO MEPC 47 by INTERTANKO, they note that for the more volatile types of crude oil, the loss rate is between 0.4 percent and 0.6 percent. A loss rate of 0.2 percent is applied in this study.

Approximately 3.3 million tonnes of petroleum products were moved by tanker vessels in 1999, including about 2.4

[7]The 33 percent factor used to develop a minimum estimate and the 100 percent factor applied to develop maximum estimate are somewhat subjective and reflects the committee's confidence in the data available and the methods and assumptions used to complete the calculation.

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million tonnes of crude oil. The estimated VOC emissions is 0.2 percent of 3.3 millions tonnes or 6.6 million tonnes per year. This is considered a conservative assumption, as the heavier products will emit significantly lower levels of VOC as compared to crude oils.

Based on the CRUCOGSA program sampling and analysis of the volatile components of approximately 1000 samples of crude oil, the VOC in the hullage space of a tanker is broken down as follows: roughly 7 percent ethane, 45 percent propane, 45 percent butane, and the remaining 3 percent of the components within the VOC emissions are heavier than butane. When released into the atmosphere, the lighter hydrocarbons will not deposit, and while it may be a "greenhouse gas" concern, does not appreciably impact the volume of oil entering the sea. Of the remaining VOC, only a small fraction is likely deposited to the sea.

To assess the potential loading of hydrocarbons from fugitive emissions of VOC, this analysis considers the following conservative calculation. The calculated value assumes that: (1) the 97 percent of the VOC released from tankers consists of light hydrocarbons that do not deposit to the sea surface; (2) the remaining VOC mix (3 percent of total VOC emitted from tankers) has a Henry's law constant equal to that of decane (which certainly underestimates its volatility and, therefore, overestimates deposition); (3) the released VOC do not react in the atmosphere or in surface waters (which ignores the substantial degradation due to hydroxyl radical attack in the troposphere); and (4) the released VOC rapidly partition between the atmosphere, which is well mixed to 1000 m altitude, and the surface ocean, which is well mixed to 100 m depth.

Assuming 3 percent of the VOC are heavier than pentane, and that 0.2 percent of these heavier compounds are deposited into the oceans, the calculated atmospheric deposition of VOC from tankers worldwide is (6.6 million tonnes) × (.03) × (.002) or approximately 400 tonnes per year. The minimum value is 200 tonnes (50 percent of the best estimate), and the maximum value is 1,000 tonnes (see Table 3-2); (300 percent of the best estimate).[8]

Within North American waters, the total cargo oil movement in 1999 was approximately 0.9 billion tonnes. In recognition of the shorter voyage lengths within coastal waters and the extensive use of vapor recovery at load ports, a loss rate of 0.01 percent is assumed, resulting in estimated VOC emissions of 90,000 tonnes. The calculated atmospheric deposition of VOC from tankers in North American waters is 5 tonnes per year. The minimum value is 2.5 tonnes (50 percent of the best estimate), and the maximum value is 15 tonnes (300 percent of the best estimate).[9] Calculation of atmospheric deposition of VOC was not included in the prior NRC reports. Given the size of the loading they may have an impact on air quality. VOC is a known pollutant and has been the subject of many NRC studies (NRC, 1992, 1995a, 1999).

Coastal Facility Spills (refined products)

Coastal facilities are defined for this report as point sources of spills that are not vessels or oil and gas exploration and production facilities (including crude oil pipelines). Table G-1 of Appendix G lists the types of facilities included in this discussion. The U.S. Coast Guard database of spills greater than 100 gallons for the ten-year period from 1990-1999 was used to estimate the amount of oil spilled from facilities. The U.S. Coast Guard data were sorted geographically to remove spills to inland waters. Also, only spills of refined petroleum products from pipelines in coastal areas were included (so as to exclude the crude oil pipeline spills from the USCG data base that were included in the section on oil and gas exploration and production). Facility spills greater than 100 gallons over the period 1990-1999 account for 9 percent of the number of spills and 98 percent of the spill volume. There was an average of 119 facility spills reported per year, with an average volume of 14.4 tonnes. Two types of facilities were the sources of 66 percent of the oil spilled over the 10-year period: coastal pipelines transporting refined products and marine terminals each were the sources of 33 percent of the spilled oil. Industrial facilities were the next largest source of spilled oil, with 14.4 percent. The pipeline spill volume was dominated by one spill event in 1994 where 5,500 tonnes of gasoline, crude oil, diesel, and jet fuel were spilled (the San Jacinto River spill in Texas). This one spill accounted for 30 percent of all the oil spilled from facilities in the 10-year period. This spill also demonstrates the problem of how to account for oil removal, since a very large fraction of the spilled oil burned.

The computed data from the U.S. Coast Guard data for North American waters resulted in estimating the minimum discharge as 1,700 tonnes per year. The best estimate is 1,900 tonnes per year (minimum + 10 percent), recognizing that spill reporting in the U.S. is very high. The maximum is 2,200 tonnes per year (minimum + 30 percent).[10]

[8]The 50 percent factor used to develop a minimum estimate and the 300 percent factor applied to develop maximum estimate are somewhat subjective and reflects the committee's confidence in the data available and the methods and assumptions used to complete the calculation.

[9]The 50 percent factor used to develop a minimum estimate and the 300 percent factor applied to develop maximum estimate are somewhat subjective and reflects the committee's confidence in the data available and the methods and assumptions used to complete the calculation.

[10]The 10 percent factor used to develop a best estimate and the 30 percent factor applied to develop maximum estimate are somewhat subjective and reflects the committee's confidence in the data available and the methods and assumptions used to complete the calculation.

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International spill data were obtained from the *Environmental Research Consulting* database and includes information gleaned from the International Maritime Organization, ITOPF, and other national and regional agencies. The minimum computed discharge is 2,400 tonnes per year, while the best estimate is 4,900 tonnes per year (minimum + 100 percent). The maximum (see Table 3-2) discharge was estimated to be 15,000 tonnes per year (minimum + 500 percent).[11]

It is difficult to compare directly these numbers to those in the NRC 1985 report because of differences in definitions. The category, marine terminals, in the 1985 report included bunkering operations, but did not specifically indicate the type of facilities included in their computation. The present report defines coastal facilities in a very broad framework (see Table G-1, Appendix G). In the NRC 1985 report, the volume discharged into marine waters by "Marine Terminals" is 20,000 tonnes per year (best estimate), with a range of 10,000 to 30,000 tonnes per year. The best estimate in this report is 4,900 tonnes per year, a significant difference existing between the two estimates.

Overall

This report, based on the methodology described in Appendix E, reports a best estimate for imports from transportation of 160,000 tonnes per year, with a minimum of 120,000 and a maximum of 260,000 tonnes per year. The categories in the NRC 1985 report included major differences from those in the present report, so no overall comparison is possible. However, operational discharges from tankers (best estimate of 36,000 tonnes per year in this report compared to 710,000 tonnes per year in the NRC 1985 report) and oil spills from tankers (best estimate of 100,000 tonnes per year in this report compared to 390,000 tonnes per year in the NRC 1985 report) indicate very significant reductions in the amounts of petroleum hydrocarbons entering the oceans from transportation-related services. In North American waters, the best estimate of petroleum hydrocarbons discharged during the marine transportation of petroleum is 9,100 tonnes per year, while the minimum is 8,500 tonnes per year and the maximum is 11,000 tonnes per year.

Consumption of Petroleum

The world population increased from 4.5 billion in 1980 to 6.0 billion in 1999, an increase of 35 percent (U.S. Census Bureau, www.census.gov). The world's merchant fleet of vessels greater than 100 gross tons (GT) increased by 18 percent, from 73,832 in 1980 to 86,817 in 1999 (Lloyds Register, 1999). There has also been a significant increase in the number and use of recreational vessels. From year 1985 to 2000, the global consumption of petroleum increased from 9.3 to 11.7 million tonnes per day, an increase of over 25 percent (www.eia.doe.gov, 2001).

Significant petroleum hydrocarbon inputs into the oceans related to consumption of petroleum include river and urban runoff, oil spills from cargo ships, operational discharges from commercial vessels and recreational craft, and atmospheric deposition of petroleum hydrocarbons. Details concerning data sources, methodology, and computations can be found in Appendix E.

Land-based (river and runoff)

Because of the scarcity of available data for estimating loads from individual sources (i.e., municipal wastewaters, non-refinery industrial discharge, refinery discharges, urban runoff, river discharges, and ocean dumping), loading estimates presented in this analysis are based on loading from all land-based sources per unit of urban land area (see Box 3-3). These calculations assumed that most of the contributions of petroleum hydrocarbons to the sea from land-based sources were from urban areas. This approach accounted for loading from all of the sources in the United States and Canada, with the exception of Gulf coast loadings from coastal refineries, which were calculated separately. The overall calculations of hydrocarbon loadings from all land-based sources for the United States and Canada were then extrapolated to other regions of the world to form a world estimate.

For the calculations in the United States and Canada, the land-based sources were divided into two categories: inland basins and coastal basins. It was assumed that inland basins discharged into major river basins that drain to the sea along the coast of the United States and Canada. Coastal basins were assumed to discharge directly to the sea. Appendix I details the methodology and calculations utilized in determining the sources of petroleum hydrocarbons to the sea from land-based sources.

In order to compute the annual average load of petroleum hydrocarbon to the sea from land-based sources, it was decided to use oil and grease (O&G) as a surrogate measure, and consider TPH and PAH to be some fraction of the O&G. The reason for using O&G data is that these data have been measured historically in urban runoff, wastewater discharges, and rivers. There is no such database available for petroleum hydrocarbon. While some PAH data are available, there is no consistency from investigator to investigator, or study to study with respect to the PAH species that were defined as comprising PAH. The method for arriving at the fractions of O&G that are petroleum hydrocarbon and PAH is described in detail in Appendixes I and J.

[11]The 100 percent factor used to develop a minimum estimate and the 500 percent factor applied to develop maximum estimate are somewhat subjective and reflects the committee's confidence in the data available (including the judgment that spills in U.S. waters are more rigorously reported) and the methods and assumptions used to complete the calculation.

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BOX 3-3

Possible Monitoring Approaches to Determine Land-Based Input

Recommendation for Monitoring Approach to Determine Land-based Inputs of Oil to the Sea

The range of uncertainty in the estimated loadings to the sea of petroleum hydrocarbons from land-based sources is four orders of magnitude. This means that it could be the largest source of petroleum hydrocarbon by a wide margin. While it is questionable whether petroleum hydrocarbons from land-based sources poses an ecological threat in the sea, the PAH fraction does, so it is recommended that both be included in a monitoring program.

It is recommended that all major rivers that have significant urban development in their watersheds be monitored for petroleum hydrocarbon and PAH at the first EPA water quality monitoring station upstream of the end of the reverse tidal flow zone. Samples should be taken monthly (or at minimum seasonally) at the bottom, mid-depth and surface of the river. It is desirable to keep the samples separate, but if cost does not permit that, they can be composited in proportion to the relative velocity of the river at the depth that each sample is taken. The river discharge must be measured at the time the samples are taken. These samples should be analyzed for the petroleum hydrocarbon and the PAH suite of compounds identified in Table 3-3, which are the compounds measured by Environment Canada. Further, these analyses should be performed on both the filtrate and residue of the filtered samples.

In addition, urban runoff and municipal wastewater effluents should be monitored in several urban coastal cities. At least one full year of sampling should be done at each site. For urban runoff a flow weighted composite sample for each storm is adequate to determine an Event Mean Concentration for the site. It is recommended that at least the following types of land use be monitored: 1) typical residential, 2) typical shopping center, and 3) urban highway with high density, slow moving rush hour traffic. Runoff samples should be filtered and the filtrate and residue analyzed for TPH and the suite of PAH compounds identified in Table 3-3.

Since not all PAH compounds are petroleum derivatives, it would be important to first determine the fraction of TPH that is PAH. Once that fraction is determined, it could be used to partition the PAH measurements in river, waste effluent and urban runoff samples into petroleum derived PAH and those derived by other sources.

The average annual load in tonnes per year of O&G was then calculated for those rivers with reported O&G concentrations by multiplying the average O&G concentration of each river by corresponding average annual flow. The average annual load for each of these rivers was then converted to unit loads per urban land area using U.S. Bureau of the Census (1998) data.

For the majority of the inland river basins, no usable O&G data were available, or observations were too few to be reliable. For these rivers, annual loading of O&G were calculated by multiplying the unit loads from the rivers for which data were available by the urban land area reported for the corresponding river watersheds in U.S. Bureau of the Census (1998) and Statistics Canada (2000).

A similar approach was used to calculate the annual loads of O&G from coastal basins. For the United States, metropolitan areas in U.S. Bureau of the Census (1998) were classified as contributing to coastal basins if they fell within one of the 451 coastal counties defined by Culliton et al. (1990).

PHOTO 9 Diffuse sources of petroleum on land contribute to rivers and runoff polluted with petroleum. Although individual releases may be very small, the cumulative load from all land-based sources accounts for about half of the total average, annual load of petroleum to the marine environment from human related activities. Thus, in terms of volume these sources far exceed the contribution from activities associated with the extraction and transportation of petroleum, combined. (Photo courtesy of Larry Roesner.)

TABLE 3-3 PAH Measured by Environment Canada

Naphthalene	Dibenzothiophene	Other PAH
C0-N	C0-D	Biphenyl
C1-N	C1-D	Acenaphthalene
C2-N	C2-D	Acenaphthene
C3-N	C3-D	Fluoranthene
C4-N	Fluorene	Pyrene
Phenanthrene	C0-F	Benz[*a*]anthracene
C0-P	C1-F	Benzo[*b*]fluoranthene
C1-P	C2-F	Benzo[*k*]fluoranthene
C2-P	C3-F	Benzo[*e*]pyrene
C3-P	Chrysene	Benzo[*a*]pyrene
C4-P	C0-C	Perylene
	C1-C	Indeno[1,2,3*cd*]pyrene
	C2-C	Dibenz[a,h]nthracene
	C3-C	Benzo[*hi*]erylene

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PHOTO 10 Barge traffic on the lower Mississippi River near New Orleans. Like other consumers of petroleum, container vessels and tug boats contribute to the chronic input of petroleum (Photo courtesy of Environmental Research Consulting.)

The individual coastal basin metropolitan areas, along with data from Statistics Canada (2000), were then aggregated into the appropriate coastal zones. The annual loads for each coastal zone were calculated by multiplying the unit loads from the rivers for which data were available by the urban land area in each coastal zone.

Because almost one-fourth of the crude oil distillation capacity of the United States is located along the Gulf coast (Radler, 1999), the petroleum refining industry discharges a substantial amount of additional O&G to coastal waters in that area. To estimate this contribution, the operating capacities for coastal refineries in Louisiana and Texas (Radler, 1999) were multiplied by an assumed rate of O&G loss that corresponded to effluent guidelines for refinery discharges. These loadings were added to the coastal discharge for the coastal zone for the western Gulf of Mexico.

The total inland river and coastal basin annual loads of O&G for the United States and Canada were summed (with the exception of coastal zones for Mexico) to give an overall estimate for North America, based on urban land area. The North American O&G loading was then extrapolated to world estimates based on the number of motor vehicles in different regions of the world (World Resources Institute, 1998).

Data on motor vehicles from the World Resources Institute (1998) were used to calculate the O&G loadings for Mexico because of a lack of data regarding urban land area for metropolitan areas in Mexico. The total load for Mexico was divided by partitioning urban areas in Mexico with populations of more than 100,000 inhabitants as of 1990 (United Nations, 1998) depending on whether urban drainage from those areas drained to the Gulf of Mexico or the Pacific Ocean.

The total petroleum hydrocarbon load was estimated as a fraction of the oil and grease load to the sea. The calculated value of land-based inputs of petroleum hydrocarbons to North American marine waters, using the unit loadings per urban land area, is 2,600 tonnes per year (minimum), while the best estimate is 54,000 tonnes per year and the maximum estimate is 1,900,000 tonnes per year (Table 3-2).[12] The worldwide best estimate, as determined using the methodol-

[12]The factors used to develop maximum and minimum estimates are somewhat subjective and reflect the committee's confidence in the data available and the methods and assumptions used to complete the calculation. As discussed in Appendix I, uncertainties regarding the percent of TPH in O&G measurements account for the vast majority of this uncertainty.

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ogy described in Appendix I, is 140,000 tonnes per year. The minimum estimate is 6,800 tonnes per year and the maximum estimate per year is 5,000,000 tonnes.

Recreational Marine Vessels

The 1985 NRC report *Oil in the Sea* did not discuss petroleum hydrocarbon inputs from operation of two- and four-stroke engines used in outboard motors and personal watercraft (PWC) (also know as jet skis) and small recreational vessels (<100 GT vessels). In both cases, there has been a significant increase in the use of recreational vessels, especially in marinas located in the coastal zone. In 1990, heightened awareness about the large number and the design inefficiencies of two-stroke engines led the U.S. EPA to begin regulating the "non-road engine" population under the authority of the Clean Air Act. Engines that fall under this category include lawn mowers, grass trimmers, chain saws, as well as outboard engines for boats. EPA has issued regulations to decrease the exhaust emissions from small marine engines by 75% by 2005 through new design features (see below). In the 1990 EPA regulations, there were only preliminary data on hydrocarbon inputs into surface water from two-stroke engines. Since then, many more studies have better quantified the inputs of hydrocarbons and gas additives such as MBTE into the air and water from two- and four-stroke engines (Jüttner et al. 1995; Barton and Fearn, 1997; M.S. Dale et al., 2000; Gabele and Pyle, 2000).

Design Features of Two- and Four-Stroke Engines

There is no pump or oil circulation system in a standard two-stroke engine, so oil is added to the gasoline to lubricate the moving parts in the engine. There is no extra valve mechanism to operate, as the piston acts as the valve, opening and closing the necessary ports. These features make these engines powerful and lightweight and therefore very popular as outboard engines on small boats.

Fuel and fuel additives that are not combusted, can enter the surface water directly with the exhaust gases through the exhaust port. Depending on how the fuel is introduced to the combustion chamber, two-strokes may emit unburned fuel and fuel additives. Before 1998, conventional two-stroke engines used either carburetors or injectors to mix fuel with air as it entered the crankcase. Since 1998, marine outboard manufacturers have been producing new, direct injected (DI) two-strokes, although the technology is still in its infancy. While there are various techniques used in DI, they all inject the fuel directly to the cylinder after or nearly after the exhaust ports close. Direct injected two-stroke engines generally have 80 percent less hydrocarbon emissions than their predecessors. In DI two-strokes, oil is introduced directly to the crankcase to lubricate the moving parts and not mixed with the fuel. As the name implies, four-stroke engines use four piston strokes for each combustion cycle including an intake stroke where fuel and air enter the combustion chamber a compression stroke combustion or power stroke and

PHOTO 11 Recreational vessels, especially those with older, two-stroke engines contribute about 6 percent of the total load of petroleum entering North American waters each year. Tri-level "boat racks" along Falmouth Harbor, in Falmouth, Massachusetts, emphasize how enjoyment of recreational marine boating has expanded, leading to a shortage of slips and vessel storage facilities. (Photo courtesy of Paul Dery.)

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exhaust stroke. These engines are designed with a separate oiling and mechanical system to operate the valves. This feature limits direct leakage of fuel, but also adds additional weight to the engine that puts them at a disadvantage as a lightweight outboard engine.

For this report, oil and gasoline inputs are calculated for standard (crankcase scavenging) two-stroke engines ranging in size from 16-175 horsepower (20-230 kW), that are fueled by a mixture of oil and gasoline. The population of engines used in recreational vessels is changing dramatically. In 1996 the EPA produced estimates on the potential impact on this changing population. However, four-stroke engines and direct-injection two-stroke engines were not included in this analysis because their populations are not adequately known. Population of other recreational vessels such as diesel outboard and inboard engines is known (EPA population model). However, aqueous fuel emissions studies have focused exclusively on gasoline engines and to our knowledge aqueous diesel emissions are not reported.

Overall, oil and gas inputs from two-stroke outboard motors are estimated to be between 0.6 to 2.5 million gallons per year (average 1.6 million gallons) or between 2,200 and 9,000 tonnes (average 5,300 tonnes) per year for coastal waters of the United States.[13]

Worldwide estimates of discharge of petroleum hydrocarbons by two-stroke engines were not estimated because of a lack of population databases. The number of two-stroke engines operational in non-North American waters, however is likely extremely large, and it is felt that this is a major source of petroleum hydrocarbons to the world's oceans.

Spills (Non-Tank Vessels)

Similar to the evaluation of tank vessel spills, the U.S. Coast Guard database was used to estimate spills from non-tank vessels in U.S. waters. During the ten-year period from 1990 to 1999, there were 1,745 spills from non-tank vessels of at least 100 gallon size. Of the recorded spills, 45 were greater than 10,000 gallons (34 tonnes) in size, and these accounted for 53 percent of the total spill volume. The average annual spillage from non-tank commercial ships was 910 tonnes per year, about 23 percent of the spillage from tank vessels.

Because comprehensive spill databases for Canadian and Mexican waters were not available, spill volumes for these waters were estimated by adjusting the U.S. figures by the relative movements of dry cargo. On this basis, the calculated oil spillage from non-tank vessels into North American waters is 1,100 tonnes per year. This figure was applied as the minimum estimate. Recognizing the completeness of the U.S. data set, the spill quantities were increased by just 5 percent to 1,200 tonnes to obtain the best estimate, and by 20 percent to 1,400 tonnes to obtain the maximum estimate.[14]

International spill data were obtained from the *Environmental Research Consulting* database and includes information gleaned from the International Maritime Organization, ITOPF, and other national and regional agencies. The international data are not collected consistently and do not include spills under 10,000 gallons (34 tonnes) in size, and are therefore regarded as underestimates. The international spill quantities were increased by 25 percent to obtain the minimum estimate, by an additional 10 percent to obtain the best estimate, and further increased by 25 percent to obtain the maximum estimate.[15] The international and North American figures were then combined to obtain the worldwide estimates of spillage from tankers. The best estimate is 7,100 tonnes; the minimum estimate is 6,500 tonnes per year and the maximum is 8,800 tonnes per year.

The NRC 1985 report used data from the International Tanker Owners Pollution Federation Ltd. (ITOPF) to estimate the quantity of oil entering the marine environment from tanker accidents. In the NRC 1985 report, the spillage from tankers was averaged over the 6-year period from 1974 to 1979, establishing a best estimate of 20,000 tonnes per year. In the IMO 1990 report, the spillage from non-tankers was not available, and a best estimate of 7,000 tonnes was made by assuming that the volume of non-tanker spills equaled 6 percent of tanker spillage. In U.S. waters, spillage from non-tankers during the period 1990-1999 was 57 percent of the spillage recorded during the period 1980-1989. It is likely that the IMO 1990 report underestimated the spills from non-tankers, and that spills from non-tankers have declined worldwide during the 1990s.

Operational Discharges (Vessels ≥100 GT)

Machinery Space Bilge Oil Discharge From Tankers

The NRC 1985 study assumed a typical motor ship with a 20,000 HP propulsion plant generated 15 gallons of bilge oil

[13]The factors used to develop maximum and minimum estimates are somewhat subjective and reflect the committee's confidence in the data available and the methods and assumptions used to complete the calculation. As discussed in Appendix F, uncertainties regarding the size of coastal populations of recreational vessels, the percent of marine vs freshwater use, and the percent of the population using new, more efficient two-stroke engine designs.

[14]Roughly 5 percent of the spills reported in the available databases did not have adequate geographic information to place them in any region with confidence. The 5 percent factor applied to develop the best estimate reflects the committee's confidence in the reporting of spills, the completeness of available databases, and a recognition that 97 percent of the total spill volume captured by these databases comes from spills that exceed 100 gallons. The likelihood that a spill much larger than that will go unobserved is, in the committee's opinion, rather small.

[15]The factors used to develop maximum and minimum estimates are somewhat subjective and reflect the committee's confidence in the data available for international waters and the methods and assumptions used to complete the calculation.

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per day. Advancements in the design of engines and pumps and the fitting of containment has reduced the quantity of bilge oil generation in modern ships, and a rate of 5 gallons per day was applied for this evaluation. The number of tankers was taken from the Lloyd's Register data for 1999, and the installed power was estimated based on the distribution of tanker sizes. Assuming 350 days per year operation, the estimated total bilge oil generation from the world's tanker fleet is 19,200 tonnes per year. MARPOL requires that the oily water effluent be discharged overboard through an oil-water separator and oil discharge monitoring system, that is set to alarm and shut down when the oil content exceeds 15 ppm. Assuming a 15 ppm oil content for bilge discharges, it is estimated that less than 0.2 percent of bilge oil is discharged overboard. Thus, if all tankers comply with MARPOL regulations, the total worldwide bilge oil discharge would be (19,200 tonnes) × (0.002), or 38 tonnes per year.

Assumed compliance with MARPOL regulations is as follows: 99 percent of tankers greater than 125,000 DWT, 95 percent of tankers 20,000 to 125,000 DWT, and 90 percent of tankers less than 20,000 DWT. Assuming non-compliant tankers discharge 100 percent of the bilge oil into the oceans, the total calculated bilge oil discharge for both MARPOL compliant and non-compliant tankers is 1,130 tonnes per year.

Machinery Space Bilge Oil Discharge From Non-Tankers

According to Lloyd's Register data there were 79,547 non-tankers above 100 GT in size operating commercially worldwide in 1999. These consisted of 38,732 commercial vessels with the main propulsion plants averaging 7,500 HP, and 40,815 other vessels with an average power of about 500 HP. Similar to tankers, a bilge oil generation rate of 5 gallons/20,000 HP was applied. Vessels between 100 GT and 400 GT, that comprise 54 percent of the non-tanker fleet, are not required to have oily water discharge equipment installed. Although these vessels are not permitted to discharge bilge effluent, it is believed that there is a significant level of non-compliance. Therefore, 15 percent of the commercial vessels and 30 percent of the other vessels were assumed not to comply with the MARPOL requirements. The total calculated worldwide bilge oil discharge for both non-compliant and compliant vessels other than tankers is 15,600 tonnes per year.

Fuel Oil Sludge From All Vessels

Based on 1998 data collected by INTERTANKO (unpublished), the world annual use of fuel oil for marine applications is estimated to be 130 million tonnes of heavy residual fuel oil and 40 million tonnes of distillate fuel. Heavy fuel oils contain between 1 percent and 5 percent sludge or waste oil, which cannot be burned as fuel and therefore must be disposed of by other means. A value of 1.5 percent is applied for these calculations. Diesel fuel oil does not produce any appreciable quantity of sludge and therefore is discounted from further consideration here. Thus, the total production of sludge from ships is estimated as (130 million tonnes) × (0.015), or 1,950,000 tonnes per year.

MARPOL prohibits the discharge of sludge at sea. The 1990 study estimated that 10 percent of tankers and 25 percent of non-tankers disposed of sludge at sea. Recognizing improvements in vessel operations and enforcement regimes and the increased use of shoreside waste reception facilities, for these calculations non-compliance is taken as 5 percent for tankers and 15 percent for non-tankers. On this basis, total discharge of sludge at sea is estimated at 260,000 tonnes per year.

Oily Ballast From Fuel Oil Tanks

Ballast discharges from fuel oil tanks are considered to be negligible. Placing seawater in fuel tanks as ballast water introduces contaminants into those tanks, increasing engine maintenance and the risk of malfunction. The practice is avoided whenever possible.

Fuel Oil and Bilge Oil Inputs Worldwide

As shown below, the total calculated operational discharge from vessels worldwide is 272,000 tonnes. Overall, the estimated discharge has not changed significantly since the 1985 report. Discharges from machinery space bilges have declined, due to improved machinery, higher levels of compliance, and the requirements for oily water separator and monitoring systems for vessels greater than 400 GT. The estimate for sludge discharge has increased, in part due to the poorer quality of modern fuels, which results in higher sludge content.

The worldwide best estimate is 270,000 tonnes. The extent of compliance is very difficult to determine, yet it has a major influence on the estimated operational discharge. Due to the high level of uncertainty, a range from 90,000 tonnes per year (one-third of the best estimate) to 810,000 tonnes per year (three times the best estimate) was assumed.[16]

Fuel Oil and Bilge Oil Inputs in North American Waters

Based on an analysis of transit miles of ships trading in U.S. waters and the size of their power plants, the generation of bilge oil on vessels greater than 100 GT in size transiting United States waters was estimated to be 2,820 tonnes. Rec-

[16]The factors used to develop maximum and minimum estimates are somewhat subjective and reflect the committee's confidence in the data available and the methods and assumptions used to complete the calculation.

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ognizing the strong controls that exist for ports in North American waters, 98 percent compliance with MARPOL regulations is assumed for vessels greater than 400 GT. For vessels between 100 GT and 400 GT, which are not required to have oil-water separators and must transfer contaminated bilge water ashore, 90 percent compliance is assumed. This results in a calculated operational discharge of 81 tonnes per year. Intentional discharge of sludge in United States and Canadian waters are assumed to be small due to the rigorous enforcement efforts, and they are accounted for in the spill data.

Factoring in Canada and Mexico, the best estimate for bilge oil discharge in North American waters is 99 tonnes per year. Similar to the worldwide estimates, the minimum and maximum values were set at one-third and three times the best estimate, respectively.[17]

Operational Discharges (Vessels <100 GT)

According to U.S. Coast Guard figures for year 2000, there were 41,313 registered vessels under 100 GT other than tankers, cargo ships, and recreational vessels. The majority of these vessels were fishing boats and small passenger vessels. The average power of these vessels was about 350 HP. It was assumed that these vessels generated 0.09 gallons of bilge oil per day, operated 50 days per year, and that 60 percent of the vessels operated in marine (non inland) waters. These estimates were the best judgment of the committee, as data were not available. Based on the above, the total bilge-oil generation in the vessels less than 100 GT was calculated to be 380 tonnes per year. Assuming a 70 percent compliance level, the best estimate of operational discharge is 110 tonnes per year. Due to the very high level of uncertainty in these calculations, a range from 23 tonnes per year (one-fifth percent of the best estimate) to 570 tonnes per year (five times the best estimate) was selected. Worldwide estimates for vessels under 100 GT were not developed due to the lack of data.

Atmospheric Deposition

In this analysis, atmospheric deposition includes wet deposition (the scavenging of hydrocarbons from the atmosphere by precipitation), dry aerosol deposition (transport of aerosol particles and their associated hydrocarbons to the sea surface), and gas exchange. In the previous NRC 1985 report, each of these three processes were recognized, but only wet and dry aerosol deposition estimates were made, due to the uncertainty in the gas exchange calculation. Because gas-exchange is likely the dominant atmospheric deposition process, estimates of its magnitude are included in this

[17]The factors used to develop maximum and minimum estimates are somewhat subjective and reflect the committee's confidence in the data available and the methods and assumptions used to complete the calculation.

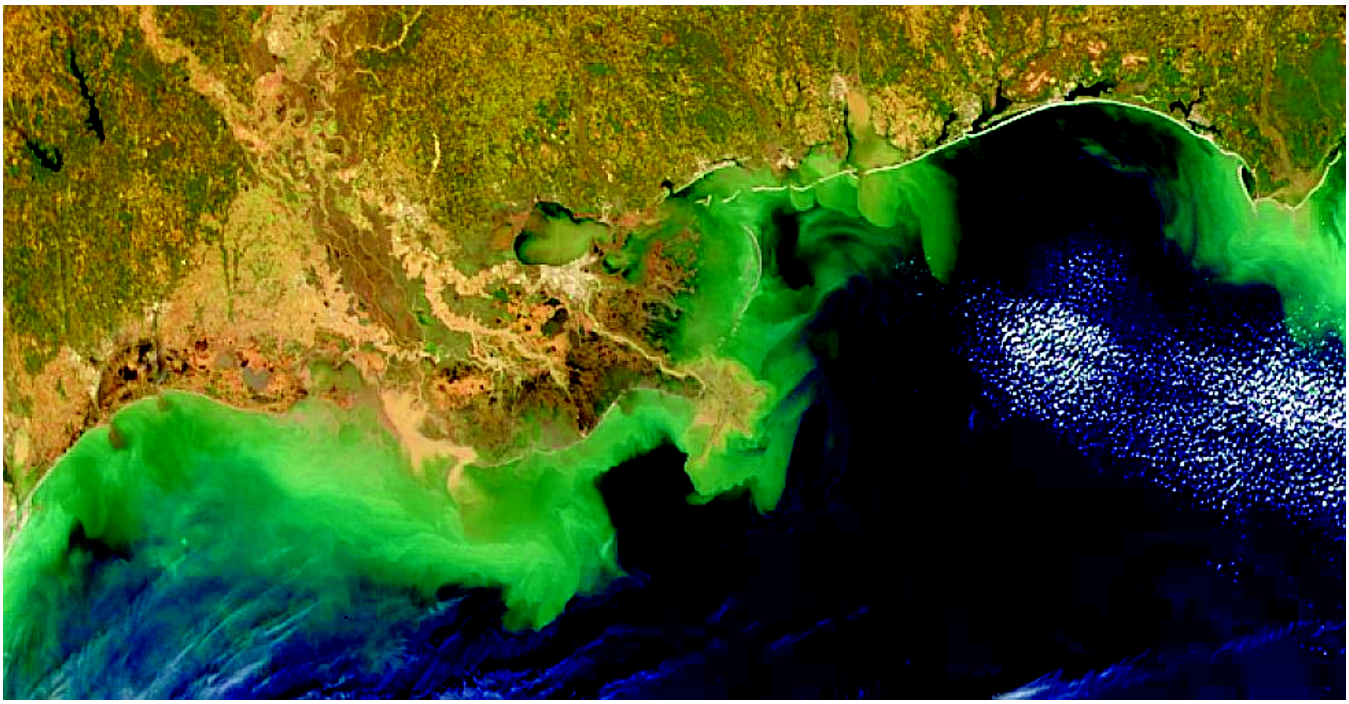

PHOTO 12 SeaWiFS (or Sea-viewing Wide Field-of-view Sensor) satellite imagery of the Mississippi River delta. As a result of high volume of tanker traffic, large number of oil and gas platforms, heavy input from the Mississippi River, and occurrence of natural oil seeps, the northwestern Gulf of Mexico experiences some of the largest average, annual inputs of petroleum to North American marine waters. (Image courtesy SeaWiFS Project, NASA/Goddard Space Flight Center and ORBIMAGE.)

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report. Gas exchange is a bi-directional diffusive flux of volatile chemicals between the dissolved phase in surface waters and the gas phase in the atmosphere. Although it is possible to mathematically separate this net flux into gross deposition (dissolution of gaseous hydrocarbons) and gross volatilization (degassing of dissolved hydrocarbons), both processes are occurring simultaneously and the net gas exchange determines both the magnitude and direction of air-water exchange.

This analysis was conducted on two spatial scales. The earlier method used by Duce and Gagosian (1982) in the 1985 NRC report, in which the world's ocean was divided into impacted (Case A) and remote (Case B) zones, was used to estimate hydrocarbon and PAH air-sea exchange worldwide. In addition, the North American coastline was divided into 17 zones, each of which was further divided into zones 0-3 miles and 3-200 miles from shore. As part of this analysis, each of these zones was described as urban-influenced or rural, and assigned consensus values for gas, aerosol particle, and dissolved hydrocarbon and PAH concentrations based on review of the literature. Deposition was assumed to be uniform within each North American zone, and the concentrations represented annual averages. Assessing seasonality, which certainly influences both the concentrations and depositional processes, was not considered in this analysis.

Ambient gas-phase, aerosol-bound, and dissolved concentrations of each hydrocarbon in the atmosphere and surface waters of each North American model segment and in the global background were estimated from the current literature. Due to the scarcity of data for the atmospheric petroleum hydrocarbons in the atmosphere bordering North America, the selection of representative distributions of PAHs and *n*-alkanes was developed from the currently available literature. For this assessment, petroleum hydrocarbons were defined as *n*-alkanes with carbon lengths ranging from C_{10} to C_{33}. To develop an accurate assessment of the contaminant burden to the coastal waters via atmospheric deposition, the various coastal structure and representative contaminant loadings had to be determined. Five zones were assembled based on the degree of urbanization along the zone's shoreline: (1) urban coastline 0-3 miles from shore (U0-3), (2) urban coastline 3-200 miles from shore (U3-200), (3) rural coastline 0-3 miles from shore (R0-3), (4) rural coastline 3-200 miles from shore (R3-200), and (5) background (BG) contaminant levels that would represent the open ocean. In most cases, adjoining 0-3 and 3-200 mile zones had the same designation (rural or urban) except along the west coast of North America, where the 3-200 zones were designated as "rural" to reflect the predominant westerly air flows off the Pacific Ocean.

Literature on atmospheric hydrocarbons in North America is sparse. This analysis began with the data used by Duce and Gagosian (1982). Published literature and known on-going studies were then used to update the estimates of hydrocarbon concentration (*n*-alkanes and PAH) in the marine atmosphere and in surface waters.

This compilation includes those endeavors that have measured concentrations in various selected areas on the United States (see Appendix H). Even fewer atmospheric *n*-alkane and PAH data were available for the North American coast that reported vapor phase alkanes per homologue (Hoff and Chan, 1987; Fraser et al., 1997, 1998). Sampling methods were somewhat consistent throughout the literature.

Methodology

Details of the methodology, databases, and computations can be found in Appendix H. Deposition models were used to estimate depositional fluxes (mass deposited per unit area per year) from these concentrations, and these fluxes were integrated over the area of each model segment to calculate the annual loading. Equations used in these calculations have been used extensively to estimate exchange of semivolatile organic chemicals between the atmosphere and surface waters (see Appendix H for equations and references). Wet deposition results from the scavenging of gases and particles, which were modeled from the temperature-corrected Henry's law constant and the aerosol scavenging ratios, respectively. Henry's Law constants for the hydrocarbons are identical to those used by Duce and Gagosian in the 1985 NRC report and were corrected to 11°C using reported enthalpies of phase change. Global annual precipitation was assumed to be 100 cm/year. While spatial and temporal variability in temperature and precipitation rate will alter atmospheric deposition rates, any bias resulting from using uniform global temperature (11°C) and precipitation rates here is likely within the error of these estimates.

Dry aerosol deposition fluxes were calculated as the product of the estimated aerosol-bound hydrocarbon and the dry deposition velocity. Estimates of deposition velocity range from <0.01 cm/sec to >1 cm/sec and depend on particle size, relative humidity, and surface turbulence. Most studies of organic chemical dry aerosol deposition suggest that a deposition velocity in the range of 0.1 cm/sec is conservative. For this analysis, a deposition velocity of 0.1 cm/sec was used, corresponding to a 0.5-μm particle depositing under average wind conditions. Annual dry deposition velocity was assumed to be spatially invariant.

Gross gas absorption deposition fluxes were calculated by dividing the estimated gas phase hydrocarbon concentrations by their respective temperature-corrected dimensionless Henry's law constants and multiplying the result by the air-sea exchange mass transfer coefficient. The mass transfer coefficient for each compound was estimated using the two-film model, applying relationships between wind speed and tracer exchange rates to parameterize surface turbulence and the compound-specific diffusivities and Henry's Law constants (see Appendix H for details and references). Gross gas deposition fluxes are only one-half of the net bidirectional diffusive exchange of gases across the air-water interface. The corresponding gross volatilization fluxes for each compound were calculated as the product of the estimated

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dissolved phase hydrocarbon concentration and the air-sea mass transfer coefficient described above. Because the analysis is calculating loads from the atmosphere to the ocean, volatilization fluxes are negative by convention.

The best estimate of atmospheric deposition (wet deposition + dry aerosol deposition + gross gas absorption) of petroleum hydrocarbons into the marine waters of North America is 21,000 tonnes per year, with a minimum of 9,100 tonnes per year and a maximum of 81,000 tonnes per year. Worldwide estimates are much larger, with the best estimate being 52,000 tonnes per year. Minimum and maximum values of 23,000 and 200,000 tonnes per year were estimated by varying the concentrations and equilibrium and mass transfer coefficients across their ranges of uncertainties. Given these loadings, there may be a regional impact on air quality.

Aircraft Dumping

There are inputs to the sea from deliberate and continual releases of fuel from aircraft. There are two sources: deliberate discharge due to emergency conditions aboard the aircraft, and normal operation releases including the release of partially burned fuel in inefficient engines or inefficient operating modes and emptying of fuel injection bypass canisters. Because of fears of dumping over residential areas, most dumping is conducted over pre-assigned areas of little habitation and in the case of airports located in coastal areas, the designated dumping region is in marine waters. Evaporation reduces the amount that directly deposits to between 5 percent and 70 percent of dump volume, depending on fuel type and weather conditions. Appendix E describes the methodology and computations of the inputs.

The computed volume of petroleum hydrocarbons dumped into North American waters is 1,000 tonnes per year (minimum). The best estimate is 1,500 tonnes per year (minimum + 50 percent), while the maximum is 4,400 tonnes per year (minimum + 340 percent).[18] Worldwide estimates range from 5,000 to 22,000, with a best estimate of 7,500.

Summary and Recommendations

The estimated range of total input of petroleum hydrocarbons from all sources into North American waters is 110,000 tonnes per year to 2,300,000 tonnes per year. The best estimate is 260,000 tonnes per year (see Table 3-2). The source with the highest contribution into the best estimate is natural seeps, being 160,000 tonnes per year or roughly 57 percent of the total. Discharge of petroleum hydrocarbons by consumers (industrial and public) is the second largest category, accounting for 90,000 tonnes per year or roughly 32 percent of the total. Spills and discharges during transportation of petroleum hydrocarbon products account for 12,100 tonnes per year (~4 percent of the total). The smallest discharge occurs during accidental spills associated with the extraction of petroleum, accounting for 3,000 tonnes per year or roughly 1 percent of the total.

The estimated range of worldwide input of petroleum hydrocarbons into the oceans from all sources is 470,000 tonnes per year to 8,400,000 tonnes per year. The best estimate from all sources is 1,300,000 tonnes per year. Natural seeps remain the largest, estimated at 600,000 tonnes per year or 46 percent of the total discharge. Activities associated with consumption of petroleum discharges is 480,000 tonnes/year or 37 percent of the total. Accidental spills and operational discharges of cargo oil occurring during transportation of petroleum products account for 160,000 tonnes per year (12 percent), while extraction processes account for 38,000 tonnes per year (3 percent).

Estimates for three significant inputs (natural seeps, land-based runoff, and operational discharges from vessels) have especially high levels of uncertainty. In particular, the maximum estimate for worldwide input from land-based runoff is more than 35 times the best estimate. For those categories with such wide ranges in uncertainty, care should be taken when applying the best estimates.

In the 1985 NRC report, the total input of petroleum hydrocarbons into the sea by all sources was estimated to be 3,200,000 tonnes per year. The inputs reported in this report are significantly lower by nearly 2 million tonnes. This has probably resulted because the databases and computational methods have improved significantly since the 1985 NRC report, and there have been worldwide efforts to stem pollution of the world's oceans. One major change between the 1985 report and the present report is the global discharge from natural seeps, 200,000 tonnes per year in 1985 and 600,000 tonnes per year in the present report. Inputs from the marine transportation of petroleum showed particular improvement. Accidental spills from tankers declined from the 1985 NRC report figure of 400,000 tonnes per year to 100,000 tonnes per year, and operational discharges of cargo oil from tankers declined from the NRC 1985 best estimate of 700,000 tonnes per year to 36,000 tonnes per year. Worldwide inputs from extraction processes are estimated to be 38,000 tonnes per year as compared to 50,000 tonnes per year in the 1985 report.

The 1985 NRC report did not report discharge by a consumption category; therefore, it is difficult to compare the figures. However, land-based runoff figures are present in both reports. In the 1985 report, the estimate was 1,180,000 tonnes per year while in the present report, the best estimate is 140,000 tonnes per year. These differences are likely related more to differences in the methodologies used to estimate the runoff than actual reductions in urban runoff of petroleum hydrocarbons. With the increases in population

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PHOTO 13 Frequent but small releases that accompany the high volume of petroleum consumed in areas with high population densities, coupled with higher percentage of paved surface leads to higher petroleum loads in surface water runoff. (Photo courtesy of Larry Roesner.)

and industrialization experienced over the last two decades, an increase in land-based runoff is expected.

Categories of inputs included in this report but not directly accounted for in the 1985 NRC report are the atmospheric deposition of VOC emitted from platforms and tankers, pipeline spills, aircraft dumping, discharges from small vessels under 100 GT in size, and discharges from recreational vessels. In particular, the operational discharges from recreational marine vessels were found to be significant.

Diffuse sources (natural seeps and run-off from land-based sources) are responsible for the majority of petroleum hydrocarbon inputs into North American waters, with contributions of 60 percent and 20 percent, respectively. In contrast, discharges from extraction and marine transportation of petroleum are responsible for less than 3 percent of the hydrocarbon inputs. Natural seeps represent the largest single petroleum hydrocarbon input, but there is a large range in the uncertainty estimation. **Federal agencies especially the USGS, MMS, and NOAA should work to develop more accurate techniques for estimating inputs from natural seeps, especially those adjacent to sensitive habitats.** Likely techniques will include remote sensing and ground truthing. This will aid in distinguishing the effects from natural processes verses anthropogenic activities.

The inputs and long-term fate of land-based sources (both due to run-off and atmospheric deposition) are poorly understood. The range of uncertainty of land-based run-off of petroleum hydrocarbons is four orders of magnitude. The upper limit, if correct, would dwarf all other inputs. The loads from rivers and air inputs are not being consistently monitored, and the background inputs from rivers are virtually unknown. **In order to assess impacts attributable to different sources including oil spills and non-point sources, federal agencies, especially the USGS and EPA should work with state and local authorities to undertake regular monitoring of TPH and PAH inputs from air and water (especially rivers and harbors) to determine background concentrations.**

For the period from 1990 to 1999, spillage from vessels in U.S. waters was less than one-third of the spillage during the prior decade, and now represents less than 2 percent of the petroleum hydrocarbon inputs into North American waters. Significant reductions in spillage were also realized worldwide. Improvements in vessel operation and design and the introduction of related federal and international regulations contributed to this decline in oil spills. In U.S. marine waters, the largest spills come from vessels, followed by pipelines and facilities. Vessels produced 109 spills greater than 34 tonnes (10,000 gallons) in size since 1990, and these larger spills had an average size of about 400 tonnes. During the 1990s, tanker vessels were responsible for about 81 percent of the spillage from vessels. The comprehensive port state control regime administered by the USCG, cooperative programs with ship owners and the boating community, and active participation at the International Maritime Organization in developing effective international regulatory stan-

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dards have contributed to the decline in oil spills and operational discharges and should be continued and further strengthened where appropriate.

Worldwide, operational discharges of cargo oil from tankers have declined dramatically over the last two decades, principally due to regulatory changes mandating segregated ballast tankers and double-hull tankers. The current best estimate is only 5 percent of the best estimate in the NRC 1985 report. Estimated operational discharges of bilge oil and sludge from vessels remain very significant inputs. Over 99 percent of the volume of operational discharges are related to estimates of non-compliance, as existing regulations restrict operational discharge of oil or limit them to not more than 15 ppm. The extent of non-compliance is difficult to assess, and therefore these estimates have a high level of uncertainty. **Federal agencies, especially the U.S. Coast Guard, should work with the transportation industry to undertake a systematic assessment of the extent of non-compliance. If estimates of non-compliance assumed in this report are essentially correct, more rigorous monitoring and enforcement policies should be developed and implemented.**

Gasoline and lube oil inputs from older, inefficient, two-stroke recreational vessels are a large marine source of petroleum hydrocarbons. These discharges are primarily gasoline and lube oil, which have high evaporation rates and low PAH levels. These inputs frequently occur near ecologically sensitive areas (estuaries, mangroves) during vulnerable stages in the life cycle of organisms. **Federal agencies, especially the EPA, should continue efforts to regulate and encourage the phase-out of inefficient two-stroke engines, and a coordinated enforcement policy should be established.**

Large quantities of VOC are discharged into the atmosphere from tank vessels and oil and gas operations. The VOC are mostly comprised of methane and ethane, which tend to oxidize rather than deposit into the oceans. These emissions may represent a "greenhouse gas" concern, but the atmospheric deposition of these hydrocarbons into North American waters is less than 0.5 percent of all inputs, and inputs of VOC into the oceans worldwide are less than 4 percent of the estimated total inputs. **The U.S. Coast Guard should work with the International Maritime Organization to assess the overall impact of VOC on air quality from tank vessels, and establish design and/or operational standards on VOC emissions where appropriate.**

On the basis of controlled data, aircraft inputs from deliberate dumping to jet fuel in the sea appear to be locally significant. **Federal agencies, especially the FAA, should work with industry to determine more rigorously the amounts of fuel dumping by aircraft and to formulate appropriate actions to limit this potential threat to the marine environment.**

PHOTO 14 The use of recreational marine vessels, including personal watercraft (e.g., jet skis), have increased dramatically in the last few decades as leisure time and access to coastal waters has increased. Unfortunately, the older, less efficient two-stroke engines powering many of these craft can contribute significantly to the total load of petroleum entering the marine environments where they are operated. (Photo courtesy of Christine Henderson.)

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4

Behavior and Fate of Oil

HIGHLIGHTS

This chapter points out the following:

- Crude oil, and refined products, in the marine environment are subject to physical, chemical, and biological processes that change their composition and environmental impact.
- The weathering of crude oil involves evaporation or volatilization, emulsification, dissolution, and oxidation (chemical, photo-, and microbial).
- The horizontal transport or movement of crude oil is accomplished through spreading, advection, dispersion, and entrainment, whereas the vertical transport of oil involves dispersion, entrainment, Langmuir circulation, sinking, overwashing, partitioning, and sedimentation.
- Crude oil from seeps and spills of persistent oils often form tar residues or tarballs that become stranded on the shoreline.
- Conceptual and computer models aid in predicting the behavior and fate of oil and oil products in the marine environment.
- The ultimate fate of oil and oil products in the environment depends on their composition, source, and persistence. Seeps, spills to surface water, deepwater subsea releases, and diffuse (non-point) sources behave in different ways.

In Chapter 3, annual loadings of petroleum hydrocarbons are estimated for each of the 16 coastal zones around North America and for the world's oceans. These loading rates, in units of mass per time, are useful in comparing the relative importance of various types of loadings and in exploring the spatial distribution of these loadings. Mass loadings, however, are not a direct indicator of the potential effects of petroleum hydrocarbons in the oceans. Ecological and human health risks generally scale to the magnitude and duration of exposure, and these mass loading rates must be translated for all hydrocarbon sources into temporally and spatially variable concentrations in the sea. Equal mass loadings to different parts of the ocean may have substantially different consequences. For example, 1,000 tonnes per year of crude oil discharged to a low-energy mangrove swamp will certainly have a much different impact than the same 1,000 tonnes per year released into the deep water of the North Sea. Similarly, equal mass loadings of different types of petroleum may result in different concentrations and potential risks. Quantitative geochemical models are used to estimate ambient hydrocarbon concentrations from mass loading estimates. This chapter discusses the many physical, chemical, and biological mechanisms that process hydrocarbon loadings once they enter the ocean. Models provide both the conceptual framework to evaluate these loadings and the deterministic tools to translate loadings into ambient concentrations and, ultimately, effects. These models combine the inherent properties of petroleum components (e.g., solubility, volatility, reactivity) with the interacting water to predict petroleum hydrocarbon concentrations. The minimum information required to translate loads into concentrations, therefore, includes knowledge of the chemical composition of the loadings and the hydrodynamics of the interacting water.

A full understanding of the impact of petroleum loadings into the ocean requires an accurate assessment of the magnitude, spatial extent, and duration of exposure. Because of the incredible diversity of physical environments within the world's oceans, it is not possible to derive simple generic relationships between petroleum mass loadings and ambient concentrations that can be applied universally. The "fate" (where it goes) and "persistence" (how long it remains in the system) of petroleum in sea water are controlled by processes that vary considerably in space and time. The processes that

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control petroleum transport (movement) in surface waters are reasonably well understood, and conceptual models exist to build deterministic models for specific loadings in a specific area for periods of time (less than one week).

Figure 4-1 shows the interrelationships among the physical, chemical, and biological processes that crude oil undergoes when introduced into the marine environment, subsequently weathers, and is then transported away from the source. Processes involved in the weathering of crude oil include evaporation, emulsification, and dissolution, whereas chemical processes focus on oxidation, particularly photooxidation. The principal biological process that affects crude oil in the marine environment is microbial oxidation. As crude oil weathers, it may also undergo various transport processes including advection and spreading, dispersion and entrainment, sinking and sedimentation, partitioning and bioavailability, and stranding which leads in some cases to tarball formation. These processes are all discussed briefly, along with special considerations of oil and ice, and oil from deepwater releases. This chapter concludes with a discussion of conceptual and computer models and a summary of fates of oil inputs to the ocean from seeps, surface spills, deepwater releases, and diffuse sources such as the atmosphere, land run off, and recreation.

PROCESSES THAT AFFECT THE IMPACT OF OIL RELEASES

Weathering

Following an oil spill or any other event that releases crude oil or crude oil products into the marine environment, weathering processes begin immediately to transform the materials into substances with physical and chemical characteristics that differ from the original source material.

Evaporation

In many oil spills, evaporation is the most important process in terms of mass balance. Within a few days following a spill, light crude oils can lose up to 75 percent of their initial volume and medium crudes up to 40 percent. In contrast, heavy or residual oils will lose no more than 10 percent of their volume in the first few days following a spill. Most oil spill behavior models include evaporation as a process and as a factor in the output of the model.

Despite the importance of the process, relatively little work has been conducted on the basic physics and chemistry of oil spill evaporation (Fingas, 1995). The particular difficulty with oil evaporation is that oil is a mixture of hundreds of compounds, and this mixture varies from source to source and over time. Much of the work described in the literature focuses on "calibrating" equations developed for water evaporation (Fingas, 1995). Initial prediction of oil evaporation was carried our by using water evaporation equations such as the one developed by Sutton (1934).

Later work of Mackay and colleagues (Mackay and Matsugu, 1973; Stiver and Mackay, 1984) was applied to describe the evaporation of crude oil through the use of mass-transfer coefficients as a function of wind speed and spill area. Stiver and Mackay (1984) further developed relationships between evaporative molar flux, mass transfer coefficient at prevailing wind speed, area of spill, vapor pressure of the bulk liquid, gas constant, and temperature.

In all of this previous work, boundary-layer regulation was assumed to be the primary mechanism for petroleum evaporation. This assumption was never tested by experimentation. Subsequently, Fingas (1995) showed that boundary regulation is slight for petroleum evaporation in the thin layers typically found on surface oil slicks, and a simple equation can be used to model evaporation:

$$\text{Percentage evaporated} = C\,(T)\ln(t), \qquad (1)$$

where C is a constant that can be empirically-determined or predicted on the basis of distillation data, T is temperature, and t is time. Empirical equations for many oils have been determined, and the equation parameters found experimentally for the evaporation of oils can be related to commonly available distillation data for the oil (Fingas, 1999). For example,

$$\text{Percentage evaporated} = 0.165\,(\text{percent D})\ln(t), \qquad (2)$$

where percent D is the percentage (by weight) distilled at 180°C and t is time in minutes, can be used for oil evaporation prediction. Figure 4-2 shows typical evaporation rates of different oils, the values of which were obtained from experiments under controlled conditions.

Emulsification

Emulsification is the process of formation of various states of water in oil, often called "chocolate mousse" or "mousse" among oil spill workers. These emulsions significantly change the properties and characteristics of spilled oil. Stable emulsions contain between 60 and 85 percent water thus expanding the volume by three to five times the original volume of spilled material. The density of the resulting emulsion can be as great as 1.03 g/mL compared to a starting density ranging from about 0.95 g/mL to as low as 0.80 g/mL. Most significantly, the viscosity of the oil typically changes from a few hundred to a few hundred thousand milli Pascal-seconds, a typical increase of three orders of magnitude. This increase in viscosity can change a liquid petroleum product into a heavy, semi-solid material. Emulsification, if it occurs, has a great effect on the behavior of oil spills at sea. As a result of emulsification, evaporation slows spreading by orders of magnitude, and the oil rides

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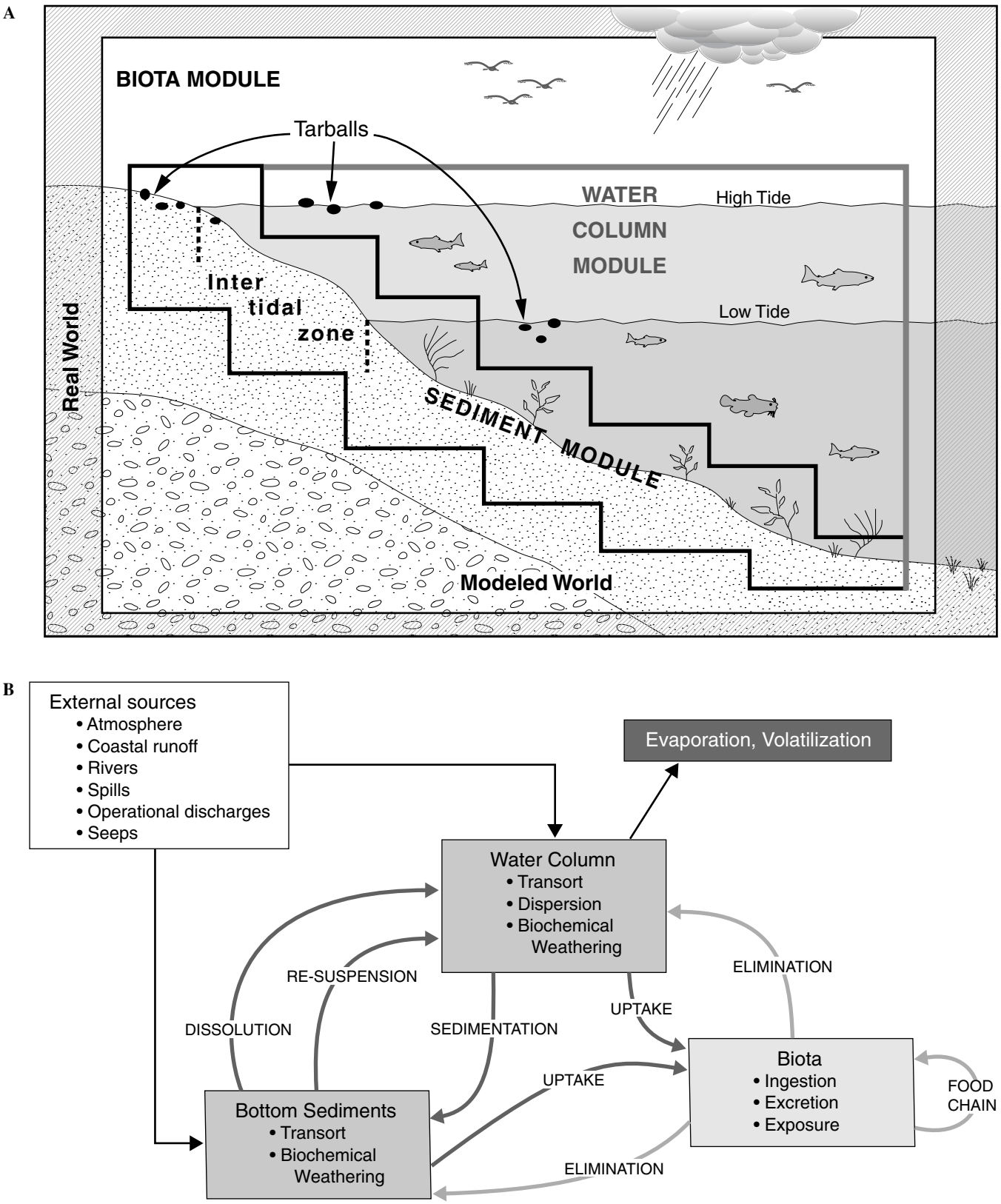

FIGURE 4-1 Graphic representation (A) and detailed interactions (B) of a conceptual model for the fate of petroleum in the marine environment. Various modules depicted are often included as significant components of computer models attempting to simulate or predict behavior and fate of petroleum compounds.

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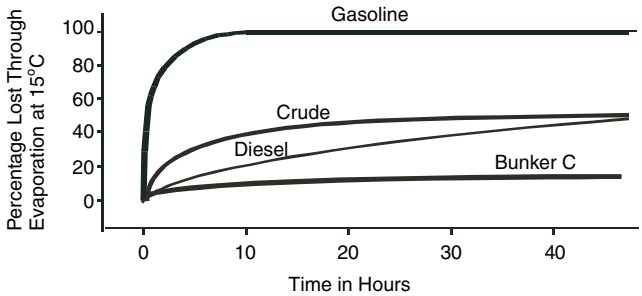

FIGURE 4-2 Evaporation rates of different types of oil at 15°C (adapted from Fingas, 2000).

lower in the water column, showing different drag with respect to the wind. Oils will generally take up water once spilled at sea, but emulsions may not always form. Water can be simply "entrained" by the oil due to viscous forces, without forming a more stable emulsion. Thus, emulsification also has significant effects on the choice of oil spill recovery methods.

In the late 1960s, Berridge et al. (1968) were the first to describe emulsification in detail. They measured several physical properties and described the emulsions as forming because of the presence of asphaltenes and resins. After these studies, there was little emphasis on the causes of emulsion formation. Mackay et al. (1982) hypothesized that emulsion stability was due to the formation of a film in oil that resisted the coalescence of water droplets; however, this work was used largely for modeling, and not for understanding, the process. Several studies have shown that water is stabilized in oil by two forces: viscous and elastic forces resulting from the interfacial action of resins and asphaltenes. This stabilization was noted as early as the 1970s when formation of emulsion correlated with the oil (Fingas et al., 1996). Only in the 1990s did studies show the effects of composition and propose clear reasons for water-in-oil emulsions. A significant factor in defining mechanisms and other characteristics of emulsions has been the development of analysis techniques for them. Sjöblom et al. (1999) have been instrumental in conducting studies on the formation of emulsions, focusing on the emulsions associated with oil production. Methods were developed to use radio-frequency conductivity to study emulsions. This group also used a Langmuir trough to show that asphaltenes formed barriers of greater strength than those formed by resins.

BOX 4-1

***T/B North Cape* Barge Spill, Rhode Island**

On January 19, 1996, the tug *Scandia* caught fire while towing the tank barge *North Cape*. The tug and tow were abandoned and storm-force winds pushed the *Scandia* ashore at the Trustom Pond National Wildlife Refuge, 3 miles west of Pt. Judith, Rhode Island. Approximately 2,850 tonnes (828,000 gallons) of home heating oil were released from the barge over a two-day period (Michel et al., 1997). Oil spread over a large area and throughout the water column, resulting in a fishing closure for approximately 250 square miles of Block Island Sound and seven coastal ponds that lasted nearly five months (Mauseth et al., 1997). This spill highlighted the conditions that occur when a light oil is released under high-wave-energy conditions, resulting in very high loading of a refined oil directly into the water column immediately after release. Thus, there was little time for traditional oil weathering processes to occur, whereby the toxicity of the oil is reduced by evaporation of the lighter, more toxic components. Two types of home heating oil were spilled, containing 3 and 6 percent polynuclear aromatic hydrocarbons (PAH), dominated by the 2- and 3-ringed PAH. An estimated 80 percent of the initial release of 700,000 gallons during the storm was physically dispersed into the water column and 12 percent evaporated in the first eight hours after each discharge. Only 10 percent of the oil was estimated to remain on the water surface in the form of sheens after the first 24 hours. Dissolved and dispersed oil concentrations in the water column reached 1-6 parts per million (ppm) total PAH. The dispersed oil droplets resurfaced during calm periods, leaving the dissolved fraction behind. The plume of dissolved oil moved along and offshore, significantly affecting benthic resources. In contrast, very little oil stranded on the shoreline, with relatively small impacts on marshes and intertidal communities, and no shoreline cleanup was necessary.

Nearshore benthic resources were greatly impacted, with estimated mortality of 9 million lobsters (mostly juveniles), 19.4 million surf clams, 7.6 million rock and hermit crabs, 4.2 million fish, and 2.8 million kilograms of amphipods and worms (NOAA et al., 1998). The extent of impacts to benthic resources was a function of the richness of the nearshore habitat, particularly for juvenile lobsters and surf clams, as well as the very cold conditions during the spill (water temperatures were 4°C). Acute mortality of benthic organisms in the salt ponds, particularly amphipods, was also estimated to be high. There were no population-level impacts on winter flounder adults who were present and spawning in the ponds at the time of maximum exposures, nor were there any growth or survival impacts for young-of-the-year winter flounder in the ponds that year.

Wildlife directly affected by the spill were seabirds and waterfowl in wintering grounds in nearshore marine waters. Of the 114 live birds collected, all but 9 died or were euthanized. The very cold conditions during the spill decreased the survival rate. Total bird mortality was estimated to be 2,300 birds (Sperduto et al., 1998). Piping plovers showed reduced productivity the breeding season after the spill (NOAA et al., 1998). The rapid weathering of the light refined oil and the absence of mixing with fine-grained sediment limited ecological impacts to short-term toxic effects on both water column and benthic resources.

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McLean et al. (1998) studied water-in-crude-oil emulsions and found that there were two stabilizating factors, viscosity and surface-active agents. Systems were studied using model emulsions with the addition of resins and asphaltenes. They found that resins and asphaltenes accumulate at the oil-water interface and form a barrier to recoalescence. Asphaltenes form more stable emulsions than those stabilized by resins alone. The state of asphaltene solubilization influences the stability of the emulsion. If aromatic solvents are in abundance, the emulsions are not as readily formed. The amounts of asphaltenes and resins were very important as are the ratios between these compound mixtures. These findings have been confirmed by a number of researchers including Sjöblom et al. (1999) and Fingas et al. (2000).

Stability is an important characteristic of a water-in-oil emulsion. Characterization of an emulsion as stable or unstable is required before other properties can be considered, because properties change significantly for each type of emulsion. Emulsion stability and four water-in-oil states: stable emulsions, meso-stable emulsions, unstable emulsions (or simply water and oil), and entrained water (Fingus, 2000; Schramm, 2000). These four states are distinguished by perseverance through time, visual appearance, and by rheological measurements. Meso-stable emulsions, which can be red to black in appearance, have properties between stable and unstable emulsions. Meso-stable emulsions lack sufficient asphaltenes to render them completely stable, although the viscosity of the oil may be high enough to stabilize some water droplets for a period of time. Meso-stable emulsions may degrade to form layers of oil and stable emulsions. Unstable emulsions are those that largely decompose to water and oil after mixing, generally within a few hours. Some water, usually less than about 10 percent, may be retained by the oil, especially if the oil is viscous. This entrained state has a short life span, but residual water, typically about 10 percent, may persist for a long time.

An important measurement to characterize water-in-oil states is forced oscillation rheometry (Fingas et al., 2000). From this measurement the presence of significant elasticity clearly defines whether a stable emulsion has been formed. Viscosity by itself can be an indicator, under some conditions, of the stability of the emulsion. Color is also used as an indicator, but it may not be definitive. All stable emulsions are usually reddish, although some meso-emulsions also have a reddish color, but unstable emulsions are always the color of the starting oil. Water content is not an indicator of stability because excess water may be present. Stable emulsions often have water contents greater than about 60 percent, whereas unstable emulsions or entrained water in oil generally have water contents less than 50 percent. Table 4-1 illustrates water-in-oil states formed from various oils under controlled laboratory conditions.

Dissolution

Dissolution is the chemical stabilization of oil components in water. Dissolution accounts for only a small portion of oil loss, but it is still considered an important behavior parameter because the soluble components of oil, particularly the smaller aromatic compounds, are more toxic to aquatic species than the aliphatic components. Modeling interest in dissolution is directed at predicting the concentrations of dissolved components in the water column. Most models in existence do not separate the dissolution component. The entrainment model is sometimes used but fails to distinguish between dispersion and dissolution.

Brookman et al. (1985) reviewed the solubility of oil and oil components in water. Most solubility data were obtained for distilled water at 25°C, using various schemes. The solubility of oil components in water varies widely depending on composition. Table 4-2 shows the solubility of very common aromatic hydrocarbons typically found in crude oils (Mackay et al., 1992). Solubility decreases very rapidly with increasing size and increasing substitution. In contrast, the solubility of the aliphatic oil components is very low relative to that of aromatic hydrocarbons and is considered to be negligible. The solubility of crude oils and petroleum products was investigated by Shiu et al. (1990) using several methods in two different laboratories and under a variety of conditions. Table 4-3 contains examples of whole oil solubilities.

The kinetics of dissolution have remained largely unstud-

TABLE 4-1 Examples of Water-in-Oil States

Oil Type	Water-In-Oil State Formed	Starting mPa.s[a]	After Formation mPa.s[a]	After One Week mPa.s[a]	Ratio of Starting/Formation
Arabian Light Crude	Stable	14	23000	23000	1640
Bunker C (15% evaporated)	Entrained	8700	28000	150000	3
Carpenteria (15% evaporated)	Meso-stable	3400	29000	20000	9
Carpenteria Crude (20% evaporated)	Unstable	160	~200	~250	~1
Dos Cuadras Crude (20% evaporated)	Meso-stable	740	9800	2500	13
Port Hueneme Crude	Entrained	4100	1600	8700	4
Sockeye	Stable	45	6900	2800000	1533

[a]Viscosity

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TABLE 4-2 Solubility of Some Aromatic Oil Components

Compound	Solubility (mg/L)
Benzene	1700
Toluene	530
Ethylbenzene	170
p-Xylene	150
Naphthalene	30
1-Methyl naphthalene	28
1.3-Dimethyl naphthalene	8
1,3,6-Trimethyl naphthalene	2
Phenanthrene	1
Fluorene	2
Dibenzothiophene	1.1
Chrysene	0.002

ied. In oil spill models, dissolution is often assumed to occur immediately (Hibbs et al., 1999). Some models have incorporated the effect of oil droplet size in the water column and used this parameter to create a kinetic behavior model (Mackay and Leinonen, 1977). In groundwater, kinetics of dissolution are often modeled using a depletion concept and based on the rate of water flow (Mackay et al., 1991).

Oxidation

Crude oil is a complex mixture of organic compounds, mostly hydrocarbons. Oxidation alters these mixtures by creating new compounds and by rearranging the distribution of residual compounds, based on their susceptibility to the oxidative process. The ultimate oxidative fate of all of the organic compounds, given an unrestricted supply of oxygen and time, is conversion to carbon dioxide and water, as expressed in the following equation:

$$CH_2O + O_2 \longleftrightarrow CO_2 + H_2O, \qquad (3)$$

where CH_2O is a symbol for all organic compounds. Not only is this the basic reaction for oxidation (to the right), it is the reaction known as "respiration" in animals and "combustion" when high temperatures are involved, and the reverse reaction (to the left) is the basic equation for photosynthesis. Hence, this reaction is fundamental to life on earth.

TABLE 4-3 Examples of Whole Oil Solubility Data

Oil Type	Solubility mg/L	Temperature °C	Salinity %
Prudhoe Bay	29	22	distilled
Lago Media	24	22	distilled
Lago Media	16.5	22	33
Diesel fuel	3	20	distilled
Diesel fuel	2.5	25	33
Bunker C	6	22	distilled
Automotive gasoline	98	22	distilled

In the oxidation of crude oil, hydrocarbons are oxidized to alcohols, ketones, and organic acids. Oxidized products are more water soluble than the hydrocarbon compounds from which they are derived. The order in which hydrocarbons are oxidized depends on a variety of factors, but in general, small molecules up to C_{20} (molecules with 20 carbon atoms or less) are oxidized before larger ones. Within the same molecular weight range, the order is the aliphatic *n*-paraffins (*n*-alkanes) first, followed by branched and cyclic alkanes (naphthalenes) and then the polycyclic aliphatic and aromatic hydrocarbons. Thus, the degree of oxidation can be ascertained on the residue, based on the type and distribution of the residual compounds. In addition, preferential oxidation of low molecular weight compounds increases the density of the unoxidized residue.

Oxidation of crude oil is mediated by two processes, photooxidation and microbial oxidation, that provide the energy to drive the oxidative reactions. Where crude oil is exposed to sunlight and oxygen in the environment, both photooxidation and aerobic microbial oxidation take place. Where oxygen and sunlight are excluded in anoxic environments, anaerobic microbial oxidation takes place.

Photooxidation in Sea Water

Photooxidation is a family of light-catalyzed reactions that oxidize the reduced carbon in petroleum hydrocarbons. These reactions include both direct photoreactions, where the reactant absorbs light energy, to form a less stable intermediate, and indirect photoreactions, where other chemical species in solution absorb light energy. Both produce reactive intermediates (e.g., solvated electrons, hydroxy radicals) that attack the hydrocarbon molecule or transfer energy directly to the reactant hydrocarbon. The necessary ingredients for photooxidation are radiation and light-absorbing molecules (chromophores). Because few petroleum hydrocarbons absorb sunlight efficiently, most photooxidation occurs via indirect photoreactions. The formation of singlet oxygen from the energy transfer of the triplet excited state of natural organic matter in sea water provides the dominant oxidant for this reaction. Heterogeneous photooxidation, in which reactions occur at the liquid-solid and liquid-liquid interfaces, may also be important. Heterogeneous photolysis of adsorbed species on natural particulate matter may result from direct photochemistry, surface semiconductor redox reactions, or photosensitized reactions on the surfaces of algal cells. Heterogeneous photolysis at the oil-water interface (i.e., surface petroleum slicks) is complex due to the large number of chromophores and reactants that change in absolute and relative abundance during photooxidation (Larsen et al., 1977; Patton et al., 1981; Payne and McNabb, 1984; Payne and Phillips, 1985). (Parker et al., 1971, cited in

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PHOTO 15 The construction of new roads and parking lots to support larger number of trucks and automobiles leads to increased runoff, runoff that often contains elevated levels of petroleum hydrocarbons. (Photo courtesy of Larry Roesner.)

Malins, 1977) Photooxidation is unimportant from a mass-balance consideration; however, products of photooxidation of petroleum slicks may be more toxic than those in the parent material (Lacaze and Villedon de NeVde, 1976). Photooxidation also plays an important role in the removal of dissolved petroleum hydrocarbons. Aliphatic and aromatic fractions of petroleum are oxidized photochemically in sunlight to more polar ketones, aldehydes, carboxylic acids, and esters. Because these products are more soluble in seawater, photooxidation enhances the overall solubilization of intact petroleum. These dissolved products can undergo further oxidative processes by either direct or indirect photolysis. In contrast, photooxidation may also result in higher-molecular-weight products through the condensation of peroxide intermediates, ultimately leading to tar and gum residues. Photochemical processes are described in detail in Zitka and Cooper (1987) and Schwarzenbach et al. (1993) and were summarized previously (NRC, 1985).

The aromatic and unsaturated fractions of dissolved petroleum hydrocarbons undergo both direct and indirect photolysis in seawater. Polycyclic aromatic hydrocarbons (PAH) degrade to relatively stable quinones via reactions initiated by electron transfer from singlet state PAH to molecular oxygen (Sigman et al., 1998). Colored natural organic matter (humic and fulvic acids) may play a role in catalyzing the indirect photolysis of PAH, both by capturing light energy and by concentrating hydrophobic PAH, within relatively nonpolar micellular environments of the macromolecules.

The extent of photooxidation depends upon (1) the spectrum and intensity of incident light, (2) the optical properties of the surface water as modified by the petroleum hydrocarbons and other dissolved and particulate constituents, (3) the optical properties of the hydrocarbons themselves, and (4) the presence of photo-quenchers and activator compounds. Petroleum photooxidation occurs faster under short-wavelength light (<300 nm) than in broad-spectrum natural sunlight. Modeling the photooxidation of petroleum hydrocarbons is complex because the surface film alters the intensity and spectrum of the incident sunlight. As weathering proceeds, individual components of the petroleum hydrocarbon mixture degrade by photooxidation at different rates and to different products, further altering the spectral environment.

Microbial Oxidation

There are generally two biological fates of petroleum in marine systems. Both utilize the same metabolic pathway, respiration, but have different end points (Figure 4-3). The first process utilizes hydrocarbons as a carbon source to produce energy, while subsequently degrading the long-chained

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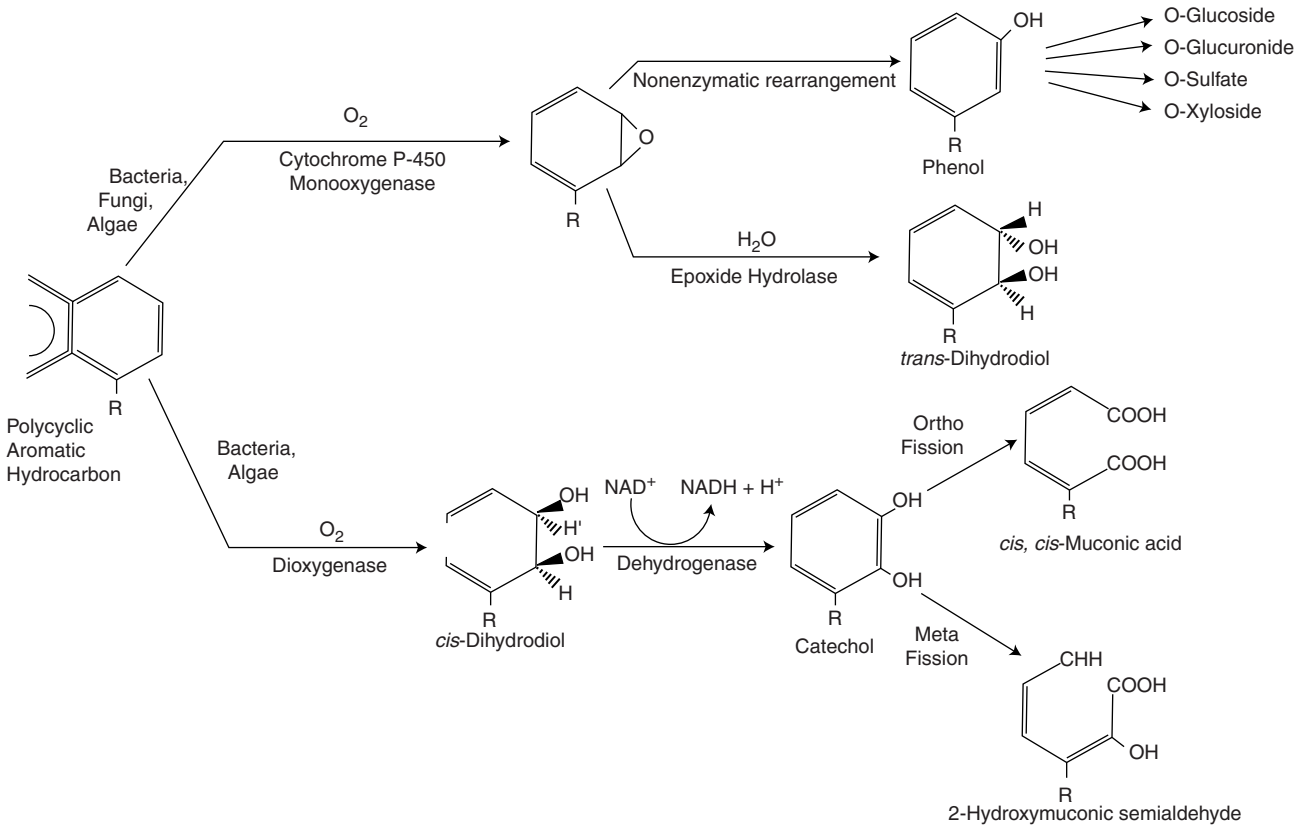

FIGURE 4-3 Two pathways for degrading PAH in oxygenated environments. Pathway one (upper) utilizes the detoxification enzyme system, cytochrome P450 1A, whereby hydrophobic PAH are oxidized to a smaller, and more water soluble molecule that can be excreted by cells. Pathway two (lower) is aerobic respiration, whereby energy in the form of adenosine triphosphate (ATP) is generated from the NADH (reduced form of nicotinamide adenine dinucleotide) produced in the breakdown of hydrocarbons. (American Insititution of Biological Sciences.)

molecules. Microorganisms, primarily bacteria and fungi, and to a lesser extent, heterotrophic phytoplankton, are responsible for these processes. The metabolic process is called oxidative phosphorylation, or respiration, and is the most energetically favorable metabolic pathway to make energy. The second biological process is primarily a detoxification mechanism in response to exposure to oil whereby an organism metabolizes the hydrocarbons to more water-soluble products that can be excreted from the body.

Biodegradation of hydrocarbons has been considered one of the principal removal mechanisms in the aquatic environment. Much of the earlier research was based on laboratory experiments that elucidated the metabolic pathways for degradation, environmental influences on oil degradation rates, and rates of oxidation. Since 1990, biodegradation of hydrocarbons has become a premiere research area as noted by at least five reviews on the topic (Leahy and Colwell, 1990; Atlas and Barth, 1992; Prince, 1993; Swannell et al., 1996; Heider et al., 1999).

There are several energetically favorable metabolic pathways to degrade hydrocarbons that are utilized by different types of microorganisms, including oxidative phosphorylation or respiration (heterotrophic bacteria, fungi, and heterotrophic phytoplankton), nitrate reduction (denitrifiers), and sulfate reduction. Complete microbial oxidation of oil produces CO_2 and H_2O often from the breakdown of smaller alkanes and cyclic hydrocarbons. More complex hydrocarbons, such as branched alkanes and multicyclic compounds (polycyclic aromatic and aliphatic hydrocarbons), require multiple metabolic pathways for degradation and likely involve a consortium of bacterial strains (Sugiura et al., 1997). Figure 4-3 summarizes two pathways for degrading PAH in oxygenated environments. Pathway one utilizes the detoxification enzyme system, cytochrome P450 1A, whereby hydrophobic PAH are oxidized to a smaller, and more water soluble molecule that can be excreted by cells. Pathway two is aerobic respiration, whereby energy in the form of adenosine triphosphate (ATP) is generated from the NADH (reduced form of nicotinamide adenine dinucleotide) produced in the breakdown of hydrocarbons.

Anaerobic degradation of hydrocarbons by sulfate- and iron-reducing bacteria has recently been measured in marine environments (Loveley et al., 1995, Coates et al., 1996). Because energy yield is relatively low, anaerobic degrada-

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tion of hydrocarbons in marine environments is limited to low-oxygen areas where heterotrophic bacteria cannot outcompete the anaerobes for carbon substrate.

Rates of biodegradation are dependent on the ability of microbes to contact hydrocarbons as well as on the bacterial metabolic processes operating within the cell. Rates of biodegradation in a natural experiment range from 50 to 100 g/m^3 per day (Lee and Levy, 1987). In the environment, rates of degradation have been reported to be between 0.001 and 60 g/m^3 per day (Atlas and Bartha, 1992). Rates for anaerobic degradation of hydrocarbons have not been measured but are generally thought to be a fraction of aerobic respiration rates. In marine environments subject to oil spills (e.g., harbors), prior exposure to hydrocarbons decreases the response times for biodegradation to occur but does not increase the rate. In more pristine environments, there is a longer time lag between the oil spill and biodegradation because the natural populations must adapt to a new carbon substrate and produce the necessary enzymes.

There is a general hierarchy for rates of biodegradation of hydrocarbons: saturated alkanes are more quickly degraded by microorganisms than aromatic compounds; alkanes and smaller-sized aromatics are degraded before branched alkanes, multi-ring and substituted aromatics, and cyclic compounds (Leahy and Colwell, 1990; Atlas and Bartha, 1992). Polar petroleum compounds such as sulfur- and nitrogen-containing species are the most resistant to microbial degradation (Prince, 1993). There are several reasons for this, including water solubility and surface area that affect their availability for bacterial adhesion and metabolism. Increasingly complex structures (e.g., branched methyl groups) and the stability of hydrocarbons decrease the rates of mineralization, which are likely a consequence of the greater stability of carbon-carbon bonds in aromatic rings than in straight-chain compounds. Emulsification (formation of small droplets) provides greater surface area for microorganisms to attach. This implies that only a certain percentage of an oil can be readily biodegraded, typically a few percent for a crude oil (over and above the percentage evaporated) and very little for a heavy oil.

Environmental factors such as oxygen concentrations, nutrients, temperature, salinity, and pressure, as well as the physical properties of oil (including surface-to-volume ratios) and the energy level of the environment, can greatly influence biodegradation rates. In addition, energy levels in marine systems, such as the physical mixing of water as well as wind and wave action, can impede biodegradation by aiding in the formation of large oil globules that have a low surface area-to-volume ratio and impede microbial cell attachment and decomposition processes. In marine systems, microorganism growth is controlled by oxygen activity, nutrient concentrations, light, temperature, salinity, and pressure. Oxygen is required for metabolism by heterotrophic bacteria and phytoplankton, as well as fungi, and is prevalent in high-energy environments where the oil-water interface is constantly aerated by the atmosphere. In addition, the marine environment is generally limited by the scarcity of the nitrogen macronutrients, and secondarily, phosphate, although site-specific and seasonal exceptions to this nutrient hierarchy abound.

Temperature can influence biodegradation. In low-temperature environments, oil viscosity increases and water solubility decreases, thereby limiting microbial attachment. In addition, volatilization of toxic, short-chained hydrocarbons is decreased and may be detrimental to microorganisms. Finally, temperature can affect cellular enzymatic activity, where the rate of enzymatic activity approximately doubles up or down with every 10°C change in temperature (the Q_{10} principle). The net effect is a decrease of biodegradation with decreased temperatures that has important implications in assessing oil spills in colder environments.

Transport

Horizontal Transport

Horizontal transport and horizontal dispersion are separate processes that stand apart from, but may enhance, spreading and Langmuir circulation. Horizontal transport means displacement along a horizontal axis, whereas, horizontal dispersion or diffusion is movement about a defined point and does not necessarily involve net movement.

Spreading

The most used models for spreading are based on the work by Fay (1969). Fay suggested that spreading is best described in three phases—inertial, viscous, and surface tension. The inertial phase is dominated by gravity forces, the viscous phase by gravity and viscosity forces, and the surface tension phase by surface tension spreading. Other models, often involving constants, have never been used extensively (Fallah and Stark, 1976). The Fay model has been subject to criticism for several reasons. First the viscosity of the water, not the oil, is used as a primary driving mechanism. Second, the model generally under-predicts spreading when tested. This observation may be explained in part as a consequence of horizontal diffusion resulting from shear diffusion of waves (Elliott, 1986).

Several tests of the Fay spreading model have been conducted. Flores et al. (1998) found that the Fay model under-predicted the spread of oil under quiescent conditions. Lehr et al. (1984) studied spreading using a series of test spills in the Arabian Gulf. They also found that the Fay model grossly under-predicted and proposed amendments to the model, suggesting that the sheen and thicker portions of the spill be modeled separately. No new formulations of the Fay spreading model have found wide acceptance; however, the formulation is often adjusted in models to account for the under-predictions shown in tests.

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Other, less common models based on work by Mackay, divide the slick into thick and thin segments that spread separately (Garcia-Martinez et al., 1996). Elliot et al. (1986) develop a spreading formula based on the shear processes cited earlier. Many models combine processes when computing their oil spread rates (Plutchak and Kolpak, 1981). The impact of these approaches in terms of modeling spill trajectories is unclear.

Advection

Few studies have been conducted on the subsurface advection of oil (Spaulding, 1995). The potential for mixing petroleum with water due to evaporation and cooling of surface waters seems limited as the buoyant forces working on the droplet tends to overcome these mechanisms. Limited modeling and observation suggest that the dissolved and particulate oil move as the bulk water moves and that the water moves in concert with mass circulation including the influence of currents and tides (Spaulding, 1995). Additional influences in the subsurface movement include vertical mixing by Langmuir circulation (McWilliams and Sullivan, 2000).

Empirical studies in the 1960s established that oil slicks on a sea surface are transported with the surface current (top centimeter of water) at 2.5 to 4 percent of the wind speed (Fallah and Stark, 1976; Reed, 1992). Furthermore, it was established that a deflection angle was appropriate to account for the Coriolis effect during slick transport. The drift velocity has largely been taken as 3.5 percent, which is the mean of the range shown above but also is a result of several carefully measured experiments (Audunson et al., 1984; Youssef and Spaulding, 1993; Reed et al., 1994). The deflection angle has been sometimes taken as 3 percent; however, Youssef and Spaulding (1993) have provided calculated values that vary with wind speed.

Langmuir Circulation

Langmuir cells (LC), often expressed as windrows, are a common feature in the sea and are generated by a wind-driven shear instability in combination with the mean Lagrangian motion from surface waves (so-called Stokes drift) as depicted in Figure 4-4. The so-called cells that compose LC have time scales of minutes and length of tens of meters. LC creates convergence and divergence zones on the sea surface running parallel to the wind vector. In the vertical, LC cause local downwelling regions that can drag surface pollutants such as oil down into the water column.

LC can potentially have many effects on surface oil. First, it enhances movement of the slick. Second, LC can create convergence and divergence zones on the surface that affect oil thickness, which in turn can affect biota, weathering rates, and cleanup strategies. Finally, LC enhances vertical dispersion of oil droplets. By pushing the droplets down into the water column, LC can indirectly affect horizontal advection and dispersion, and increase the amount of hydrocarbon that dissolves into the water column.

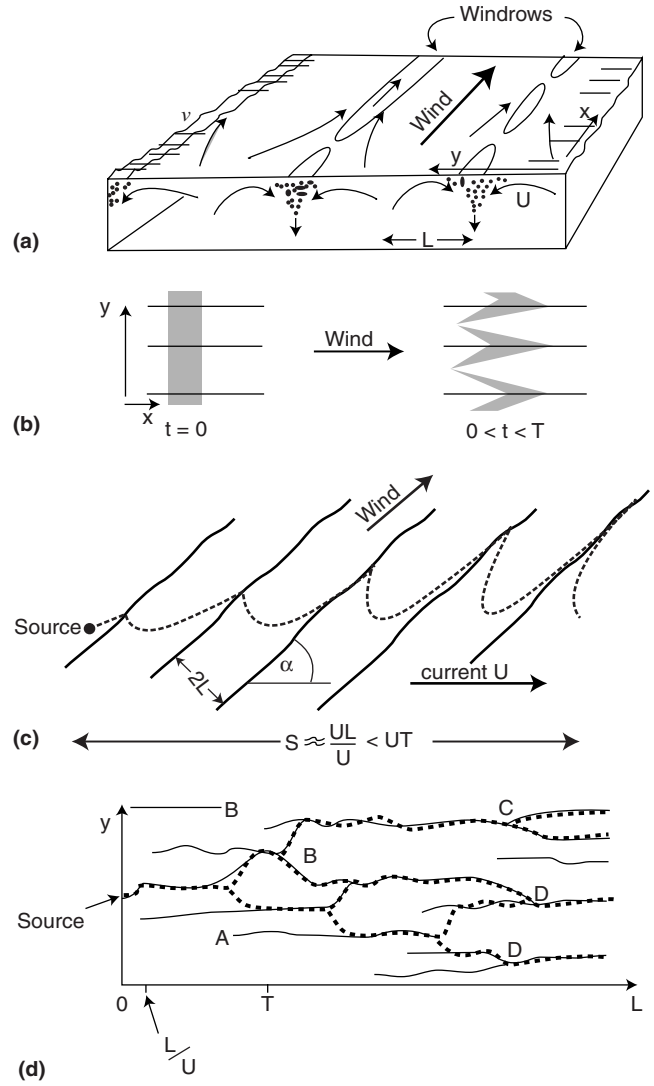

FIGURE 4-4 Diagram of Langmuir Circulation (LC) showing (a) perspective sketch of some of the features of LC (Note regions of convergence on the surface and characteristic length scale of the cells is "L" in the vertical and horizontal); (b) longitudinal dispersion and advection of floating particles by Langmuir circulation. A rectangular cloud of particles is shown at the start of LC motion (t=0) and after some time but before LC breaks us (t=T); (c) advective dispersion of a plume of seed particles when the wind and current angles are inclined at angle, a; and, (d) dispersion of seed particles at LC break-up or instability. (Modified from Thorpe, 2001, Elsevier Science, Inc.)

McWilliams and Sullivan (2001) compare the LC enhancement of vertical and horizontal dispersion and argue persuasively that vertical dispersion is the most important. They argue that since the characteristic mixing length of LC

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PHOTO 16 A spill of roughly 320,000 gallons of south Louisiana crude in May 1997, streaming across the broken marshes of Lake Barre. There is very little substrate exposed thus the oil is being pushed through the submerged vegetation by wind. (Photo courtesy of Jacqui Michel, Research Planning, Inc.)

is the same in both the vertical and the horizontal (order of tens of meters), the vertical component is more important because it is strong compared to other normal vertical mixing processes in the ocean. In contrast, LC-induced horizontal dispersion is weak compared to other horizontal mixing processes. Rye (2001) shows aircraft observations from numerous spills that indicate LC horizontal dispersion, but the effects are relatively small scale. It is interesting to note that Rye's (2001) comparison focused solely on horizontal scales and not vertical, presumably because of the lack of good data in the vertical.

Lehr and Simecek-Beatty (2001) point out that LC may well be as important at enhancing vertical dispersion as wave breaking. Theory suggests that wave breaking will drive oil droplets roughly one wave height into the water column, whereas LC could drive smaller near-neutrally buoyant droplets tens of meters down, perhaps as far as the base of the mixed layer. Given this, it is an apparent paradox that state-of-the-art oil spill trajectory models include vertical dispersion due to wave breaking but not LC. The primary reason for this is that there is presently no relatively simple verified algorithm to include LC in a spill model. A realistic model would have to not only include a physical model of the Langmuir cell hydrodynamics but also to consider the buoyancy of the oil droplets and hence the droplet-sized distribution. None of these are well understood.

In summary, LC is a potentially important mechanism whose effects have been seen in real spills but are not presently well understood. Further measurements are clearly needed especially with regard to the efficiency of LC in enhancing vertical dispersion and subsequent hydrocarbon dissolution. If further research demonstrates the importance of LC compared to other processes, then a relatively simple LC algorithm should be developed and incorporated into oil spill trajectory models. LC effects on cleanup strategies are another potentially fruitful topic of research.

Horizontal Dispersion

Dispersion is a mixing process caused by the turbulence field in the ocean. It is the process that would cause a liter of instantaneously released dyed water to expand over time and eventually dissipate in the ocean. Without dispersion, advection would move that liter downstream, but the volume of dyed water would not change over time. Dispersion occurs in both the horizontal and the vertical directions, but because the hydrodynamic processes in the vertical and horizontal are often quite different, a distinction is usually made.

In oil spill modeling, horizontal dispersion is often combined with "spreading," but they are fundamentally different processes characterized by different length and time scales. A liter of oil dumped on a tabletop will spread but it will not

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disperse. Although spreading and horizontal dispersion start to work immediately after a spill occurs, spreading is nearly complete within a day while dispersion continues to increase. For most offshore spills, dispersion will move more oil around than will spreading.

Dispersion originates from ocean eddies of various scales, Langmuir circulation, boundary-layer shear (e.g., wind gusts blowing on the sea surface), and other seemingly random turbulence. Dispersion is typically modeled using a Fickian law that assumes a neutrally buoyant, noncohesive substance. Clearly oil is different, so at the very least the dispersion coefficients used in a Fickian model will likely be different from those determined for miscible substances. Some composite oil slick models simply ignore horizontal dispersion and focus on the "center of mass" of the slicks. The National Oceanic and Atmospheric Administration's GNOME model uses a Fickian law. Others have developed heuristic methods with coefficients tuned to observed slick data. Examples include Morales et al. (1997) who have developed a random-walk method and Howlett et al. (1993) who break the spill into parcels called "spillets" and disperse them numerically.

Vertical Dispersion and Entrainment

Vertical dispersion and entrainment are the movements of oil droplets of sizes less than about 100 μm into the water column. Typically droplets that display a residence time of minutes to hours have droplet sizes less than about 20 μm (Reed, 1992). Larger droplets will rise quickly to the surface. MacKay developed an early model of entrainment based on the square of wind speed, the viscosity of oil, slick thickness, and surface tension (Reed, 1992; ASCE, 1996). Tests of this model showed that it provided reasonable results at moderate wind speeds, but otherwise deviated from experimental values.

Delvigne et al. (1987) and Delvigne (1993) developed a series of models based on a number of different flume tests, tank tests, and at-sea measurements. These commonly used models are empirical and are based on breaking wave energy, film thickness, oil type, and temperature. Energy is included as turbulent energy dissipation by the waves per unit area. Later models were developed to account for energy applied by other than breaking waves and included movement around obstacles and hydraulic jumps. The models have been applied successfully under a variety of circumstances. They do not, however, account for the stability of the droplets in the water column, a factor that largely depends on droplet size and has been modeled based on empirical data (Delvigne et al., 1987). Few tests of models have been done at sea because of the analytical difficulties of measuring the many factors involved. The tests conducted thus far have been mainly an extrapolation of the fate of oil to the Delvigne model (ASCE, 1996). The depth of mixing was found to conform largely to the rule of thumb that states that the depth of mixing is 1.5 times the wave height (Delvigne et al., 1987).

Sinking and Sedimentation

Sinking is the mechanism by which oil masses that are denser than the receiving water are transported to the bottom. The oil itself may be denser than water, or it may have incorporated enough sediment to become denser than water. Sedimentation is the sorption of oil to suspended sediments that eventually settle out of the water column and accumulate on the seafloor. There is a significant difference in the relative amount of oil incorporated by the two processes; sinking oil may contain a few percent sediment, whereas contaminated sediments accumulating on the seafloor will contain at most a few percent oil (McCourt and Shier, 2001). Sedimentation requires a mechanism for oil to become attached to sediments. One mechanism is ingestion of small oil droplets dispersed in the water column by zooplankton and excretion of oil in fecal pellets that then sink to the seafloor. This process has been documented only during the Arrow spill in Chedabucto Bay (Conover, 1971).

The National Research Council (NRC, 1999) developed conceptual behavior models for nonfloating oils that described the factors determining whether spilled oil will sink. Figure 4-5 shows the interaction of these factors. Because most nonfloating oils are only slightly denser than water, the presence of currents can keep the oil in suspension and prevent its accumulation as a coherent mass on the bottom. For example, little or no oil accumulation on the bottom was reported after heavy-oil spills in the Mississippi River (Weems et al., 1997) and Puget Sound (Yaroch and Reiter, 1989). In very few spills of oil that was heavier than water, the oil sank directly to the bottom, and these kinds of spills occurred only in sheltered settings (e.g., from the vessels *Sansinena* and *Mobiloil*). In contrast, a buoyant oil can pick up enough sediment, either after stranding onshore or mixing with sediment suspended by wave action, to become an oil-sediment mixture that is denser than sea water. If the sediment separates from the oil mass, the still-buoyant oil can then re-float, as was observed at the *Morris J. Berman* spill in 1991 in Puerto Rico.

Recent studies on sedimentation of spilled oil have focused on the interaction of fine particles (clay) and oil stranded on the shoreline as a mechanism that speeds natural removal of residual stranded oil (Bragg and Owens, 1995). This process involves oil-fine interaction of micron-sized mineral fines with oil droplets in the presence of water containing ions. Once processed, the oil droplets do not coalesce, and the oil is readily removed from the shoreline by tidal flushing and wave action. The oil-clay oil particle clusters are of near-neutral buoyancy and are easily kept in suspension. The oil attached to the fine particles is more available for biodegradation. This process was first described during the *Exxon Valdez* oil spill and has been proposed as occurring at other recent spills (Bragg and Owens, 1995). No field or laboratory measurement techniques, however, have been developed that enable immediate identification of

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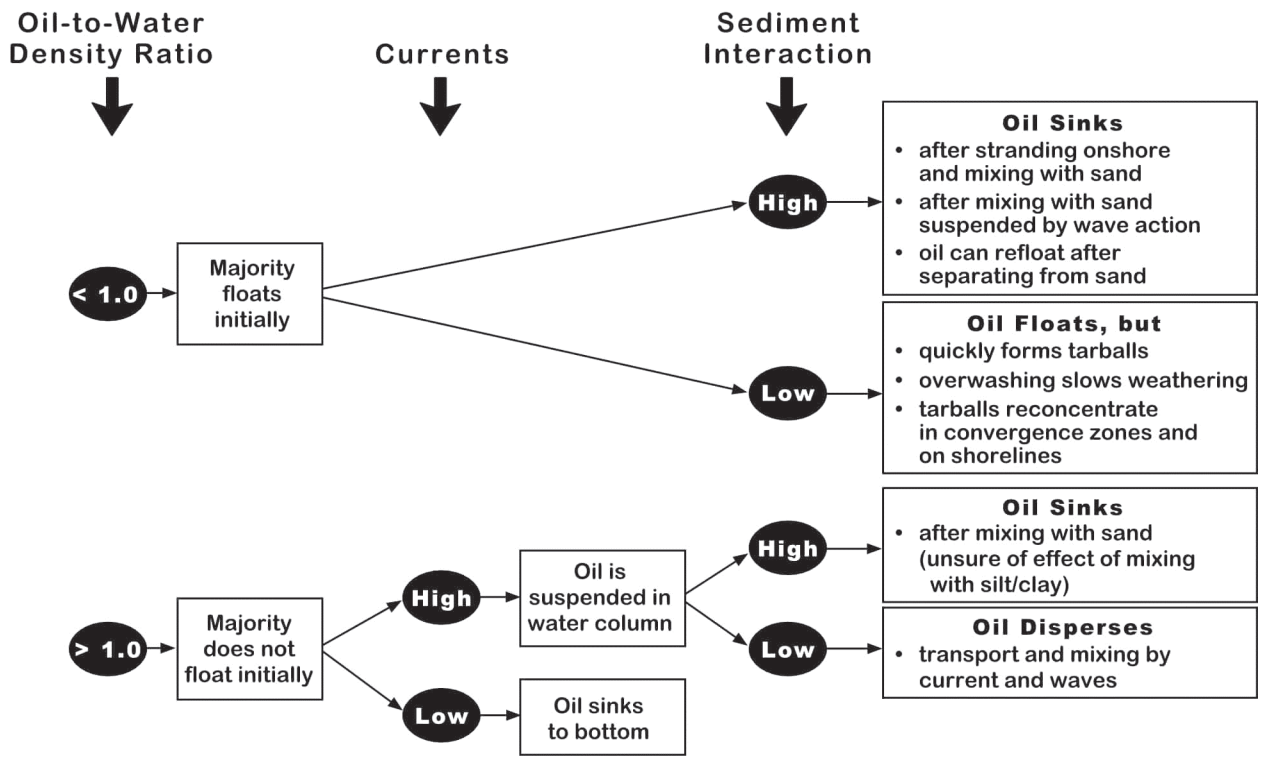

FIGURE 4-5 Factors determining whether spilled oil will float or sink (NRC, 1999).

the process or the potential for the process to occur in a spill situation. Recent work on oil-fines interaction stimulated new research on the interaction of oil and suspended solids in glacier-fed rivers in Alaska. In laboratory mixing tests with water from eight rivers collected over three seasons in Alaska, oil-sediment interactions occurred, but the factors controlling the amount of oil loading could not be identified (McCourt and Shier, 2001).

Overwashing

Overwashing is the temporary submergence of oil below the water surface. The oil can be described as "floating" just below the water surface. Environment Canada conducted several studies in the 1980s to investigate the factors influencing oil submergence as part of an overall program on the behavior of spilled oil (Wilson et al., 1986; Clark et al., 1987; Lee et al., 1989). Equations for overwashing were developed by Mackay et al. (1986) and have been used in some models to predict this process. There have been no significant advances in the theory of overwashing since this work.

The principal cause of overwashing is the action of waves and near-surface turbulence (Clark et al., 1987). Two other factors are also very important: the density of the oil must be close to that of water and the oil must become viscous enough so that the slick breaks up into discrete masses such as tarballs (Buist and Potter, 1987).

Overwashing is particularly important because submerged oil is difficult to see visually or with remote sensors, making it difficult to detect the oil, track its path, and make accurate trajectory predictions. During the *Nestucca* spill, the oil broke into tarballs that became overwashed and could not be visually tracked. Two weeks later, the oil showed up along 150 km of shoreline on Vancouver Island, Canada (NOAA, 1992). Submerged oil also weathers more slowly because there is almost always a thin water layer on top of the oil (Clark et al., 1987). Thus, relatively fresh oil can travel hundreds of kilometers from the release site. Finally, it is very difficult to recover submerged oil using standard skimming equipment.

There are three mechanisms by which submerged oil can resurface: (1) the density of the water increases, as in an estuary where the oil moves from fresh water to salt water; (2) the turbulence of the water surface ceases, when the wind dies down or a river plume enters a bay; and (3) the oil becomes stranded on a shoreline.

Partitioning and Bioavailability

Partitioning

Petroleum hydrocarbons come in many chemical forms or species and partition among the myriad particulate and

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dissolved phases of surface sea water including minerals (e.g., iron oxides) and live and dead cells. These partitioning processes include adsorption where the hydrocarbon attaches to the two-dimensional surface of a solid or other interface and absorption where the chemical partitions into the interior of a cell or detrital particle. Understanding the distribution of petroleum hydrocarbons between the dissolved phase and the variety of aquatic particles is important for determining the fate of hydrocarbons in the sea and the bioavailability of these chemicals to marine biota.

For nonpolar organic chemicals, including most of the components of petroleum, the science of partitioning is based on early studies of pesticide retention by soils, which formed the basis for later work with sediments. This field has been extensively reviewed and synthesized (e.g., Karickhoff, 1984; Schwartzenbach et al., 1993; Chiou et al., 1998; Stangroom et al., 2000). For these compounds, associations with solids result primarily from nonspecific interactions with the solids, often driven by hydrophobic exclusion from the dissolved-phase. The simplest model of dissolved-solid distributions is the equilibrium isotherm. The concentration of a solid-associated chemical is related to the dissolved phase concentration by an equilibrium constant $K = C_p/C_d$, where C_p is the solid-associated concentration of a chemical (mass of chemical per unit mass of solid) and C_d is the thermodynamically dissolved concentration. (In practice, "dissolved" is an operational definition corresponding to the water fraction that can pass through a 0.2 or 0.45 μm membrane filter and includes solids such as minerals, bacteria cells, and colloids; in these cases, the true equilibrium partition coefficient, K, is approximated by a distribution coefficient, K_p.) For nonpolar compounds, the magnitude of K is inversely proportional to the compound's aqueous solubility and is directly proportional to the octanol-water partition coefficient (K_{ow}). Furthermore, K varies with the nature of the solid phase, especially the fractional organic carbon content and grain size.

Since the NRC (1985) report, there have been great advances in analytical measurements of the different fractions and in predicting the dissolved-solid distributions and bioavailability of hydrocarbons, especially PAH. Initially, partitioning of PAH was modeled as an equilibrium process, based on laboratory observations that the distribution of hydrocarbons apparently reached constant conditions after a few hours. Subsequent work established that desorption may be much slower that adsorption, especially after the sorbed chemical has been allowed to age within the solid (Karickhoff, 1984; Wu and Gschwend, 1988; Ball and Roberts, 1991; Huang et al., 1998; Kan et al., 1998, 2000). Slow desorption has important implications for the fate and transport of hydrocarbons, both in surface waters and in the subsurface environment (Mackay et al., 1986). For example, concentrations of PAH attached to particles from land-based sources may be supersaturated with respect to the corresponding dissolved phase in coastal waters, resulting in a desorption gradient driven by diffusion. The extent to which this disequilibrium will persist depends on the relative rate of desorption compared to the residence time of the particle in the coastal waters As another example, the amount of hydrocarbon released from contaminated sediments that are resuspended into the water column as a result of storms, tides, or dredging depends directly on the desorption rate. Also, the surface to volume ratios (S:V) of laboratory studies should be considered when evaluating field conditions, and compared with the S:V of oils occupying different environments. During the past 15 years, kinetic adsorption-desorption algorithms that describe rate processes have begun to find their way into newer hydrocarbon fate and transport models. Most commonly used "off-the-shelf" modeling packages continue to employ equilibrium partitioning.

Another significant improvement in the description of dissolved-solid partitioning is the recognition that highly sorbing phases within aquatic particle populations can greatly reduce hydrocarbon bioavailability and reactivity in the marine environment. The presence of soot particles in coastal marine sediments significantly alters the partitioning of PAH between sediments and porewater (McGroddy and Farrington, 1995; Gustaffson et al., 1997a; Naes et al., 1998). Whether this alteration is due to highly energetic adsorption sites on the soot particle surfaces or to correspondingly slow desorption kinetics from these particles (or, more likely, both) is not yet clear. This strong binding within the sediments likely decreases the availability of PAH to benthic organisms (Maruya et al., 1996; Naes et al., 1998; Lamoureux and Brownawell, 1999; Krauss et al., 2000). The composition of sedimentary organic matter also affects the efficiency with which benthic organisms extract PAH from sediments (Landrum et al., 1997; Standley, 1997; Weston and Mayer, 1998; Baumard et al., 1999).

Bioavailability

Organisms are exposed to petroleum hydrocarbons in the marine environment. They are not exposed to the total amount of hydrocarbons in the water and sediment, however, because some portions of the chemical occur in forms not accessible to the organisms. The processes controlling bioavailability have been reviewed by. Partitioning strongly affects the mechanisms and magnitude of exposure of aquatic organisms to hydrocarbons. Dissolved hydrocarbons can diffuse across gill and cell membrane surfaces, and those associated with particles can be ingested during feeding. If oil droplets are present in the water column, marine filter feeders are exposed to PAH by direct uptake of the oil (Menon and Menon, 1999). Unlike other nonpolar compounds such as polychlorinated biphenols (PCBs) and certain pesticides, PAH sometimes bioaccumulate in the food chain depending on the metabolic rate of the organism.

Single-cell organisms, such as phytoplankton, are exposed to hydrocarbons primarily through partitioning of dis-

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PHOTO 17 Oil on intertidal flat in Saudi Arabia in May 1991. The heavy oil slicks persisted long enough (for months) in protected bays to coat the entire intertidal zone. (Photo courtesy of Jacqui Michel, Research Planning, Inc.)

solved hydrocarbons, operationally defined as passing through a 0.2-μm filter and including colloids and small particles. Any geochemical process that decreases the dissolved hydrocarbon concentration, including partitioning onto larger solids, will reduce hydrocarbon exposure of phytoplankton. Conversely, partitioning of hydrocarbons onto organic-rich particles, including plankton and detritus, results in transfer of hydrocarbons to higher trophic levels, including filter feeders (e.g. mussels, oysters), fish, and mammals. The extent of hydrocarbon accumulation in organisms is controlled by the desorption rate of hydrocarbons from particles in the gut (for higher trophic organisms) and metabolic rates that degrade or transfer hydrocarbons outside the cell.

Shoreline Stranding and Tarball Formation

Persistent oil residues have two major fates: shoreline stranding for spills near to shore and tarball formation for releases in offshore waters. Oil loading on a shoreline can be highly variable, and the amount of oil and the rate of natural removal drive the decision to conduct shoreline cleanup. The sensitivity of shorelines to oil has been embodied in a ranking system called the Environmental Sensitivity Index (ESI) that has been widely applied for oil spill planning and cleanup decision-making (Halls et al., 1997; Hayes et al., 1980); (see Box 2-2). The ESI classifies and ranks shorelines according to the factors that influence oil persistence and impacts, such as degree of exposure, substrate permeability, and shoreline slope. Highest on the scale are the sheltered habitats, such as muddy tidal flats, marshes, and mangroves. These shoreline types are usually priority areas for protection because of their sensitivity and the difficulty of cleanup. Gravel beaches have the highest ranking for beaches because their high permeability allows deep penetration, complex patterns for sediment reworking during storms, low rates of natural replenishment, and the presence of localized, sheltered areas where oil can persist for years (Hayes and Michel, 2001). Decision-making for shoreline cleanup must evaluate the trade-offs between the impact of the oil and the impact of the cleanup. The objective is oil removal to the point that allows recovery without causing more harm than leaving the oil in place (NOAA, 2000). There are well-established guidelines for shoreline assessment, cleanup methods, and cleanup end points (NOAA, 2000; Environment Canada, 2000).

A coastal zone oil spill model (COZOIL) was developed to predict the behavior, loading, and fate of oil stranded on different shoreline types (Reed and Gundlach, 1989). It considers the oil density, viscosity, wave energy, grain size of

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shoreline sediments, and empirical holding thicknesses, penetration depths, and removal coefficients for each type of shoreline. This work provided the algorithms needed to improve the accuracy of oil fate models that previously did not fully consider the amount of oil stranded on a shoreline.

As a result of the various physical and chemical processes that affect floating oil from seeps, spills, and operational discharges (e.g., discharge of ballast water), oil can eventually coagulate into residues called tarballs. While some tarballs may be as large as pancakes, most are coin sized. Spills of heavy oils often quickly break into patches of tarballs, making them difficult to track. Tarballs are very persistent in the marine environment and can travel hundreds of miles, sometimes reconcentrating in convergence zones far from the original spill site. Tarballs are problematic because of their long-term persistence and ubiquitous nature along shipping routes (see Plummer, 1996; Butler et al., 1998; Gabche et al., 1998).

Natural oil seeps, which release small amounts of oil over long periods of time (thousands of years) have also caused contamination of beaches, particularly in southern California (Landes, 1973), and naturally occurring tarballs in the Gulf of Mexico and the Caribbean have been described in detail (Geyer and Giammona, 1980). Anthropogenic pollution of beaches began in the twentieth century with the increased shipment of crude oil and refined petroleum products by sea. Thus, coastal locations near natural oil seeps and/or tanker traffic routes are likely candidates for impact by tarballs that continue to contaminate many coastlines worldwide (Butler and Morris, 1974; Hiffe and Knap, 1979; Knap et al., 1980; IOC, 1984; Smith and Knap, 1985; Atwood et al., 1987a,b; GESAMP, 1993; Butler et al., 1998).

Biomarkers (organic compounds whose structure reflects the biological source) and isotope geochemistry (mainly ^{13}C) have been widely applied to characterize tarballs and to differentiate anthropogenic from natural sources, as well as to discriminate among the many possible subsources of anthropogenic contamination. For example, oil pollution in the Straits of Malacca was determined by biomarkers to be from Middle East and South Asia crude oils (Zakaria et al., 2000). In the eastern Mediterranean, biomarkers differentiated four different oil types in tar residues on the coast at Sidi Heneish, 240 km west of Alexandria, Egypt (Barakat et al., 1999). Biomarkers and carbon isotopic compositions were also used to show that crude oil had been spilled in Prince William Sound before the *Exxon Valdez* spill in 1989 (Box 1-1). In fact, the spill likely occurred in 1964 as a result of the Great Alaska Earthquake during which stored oil, originally shipped from California, was inadvertently released into Prince William Sound when storage facilities were destroyed (Kvenvolden et al., 1995).

The sources of tarballs remain a global coastal contamination issue; thus, continued efforts should be made to develop analytical tools and parameters to enhance the identification of sources. Systematic monitoring of ocean-facing beaches, as recommended by Butler et al. (1998), should continue and be augmented as an inexpensive means to verify changes in pollution input from shipping and the effectiveness of international laws. In addition, efforts to distinguish anthropogenic and natural crude oil contamination of coastlines should continue so that the role of natural seepages, over which humankind has little control, and anthropogenic spills of crude oil and refined products, which humankind is able to minimize, can be readily and accurately distinguished.

Oil and Ice

The behavior and fate of oil in the Arctic, and in other ice-containing marine environments, is modified by the presence of the ice and by the lower temperature (Fingas and Hollebone, 2001). The different ice conditions largely dictate the fate and behavior of oil in a specific situation. The relevant ice conditions can be considered as the following: pack and other ice on water, in leads, with frazil/grease/brash ice, under ice, encapsulated in ice, on ice, and on snow. Several of these have subconditions that significantly change the way oil behaves in the Arctic environment. The amount of ice present on water influences the behavior of oil significantly; generally more than three-tenths (i.e., 30 percent) ice coverage is taken as a condition in which the behavior of oil changes significantly over an open water condition. The behavior of oil under ice differs significantly if the ice is first-year or multiyear ice. First-year ice contains micro-channels with concentrated brine formed by the exclusion of the salt during ice formation. During spring, these brine channels drain and allow oil under or in the ice to rise to the surface. Table 4-4 summarizes the important behavior and fate processes that are modified by the presence of ice and cold.

Several behavioral modes are affected by the presence of ice or the lower temperature in the Arctic. The evaporation rate is reduced by the lower temperature. The extent of evaporation of the oil is not the same as that of warmer climates and is, in addition, slowed by adsorption to snow or ice. Ice-encapsulated oil does not evaporate. Emulsification of oil in Arctic environments has not been fully studied; however, it is believed to occur as readily as it would in other environments. The increased viscosity of the oil at lower temperatures would, in many cases, enhance the formation of water-in-oil emulsions. Although ice on the water damps waves, there is often sufficient sea energy of water interaction with ice to form emulsions. An important aspect of the behavior of oil in the Arctic is adhesion to snow and ice. The effect of adhesion is to remove the oil from other immediate processes to which it might be subjected. For example, oil that adheres to ice edges will no longer spread, nor is it likely to emulsify. Another result of adhesion is to contain the oil initially, but later to spread it out over a larger area. Because the outer edge of the ice pack is very dynamic as is the first-year ice upon breakup, oiled ice can spread over a long dis-

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TABLE 4-4 Behavior Modes Influenced by the Presence of Ice

Location	Sublocation	Behavior mode
On water	<3/10 ice cover	as open water
	>3/10 ice cover	spreading evaporation adhesion to ice
	In leads	spreading and evaporation as above pumping to ice surface
	With frazil/grease/ brash ice	spreading adhesion to ice
Under ice	Under first year ice	spreading evaporation rise to surface through brine channels
	Under multiyear ice	spreading and evaporation as above rise to surface through channels
In ice	Encapsulated	evaporation rise to surface
On ice	On ice	spreading evaporation pooling
	Under snow	spreading evaporation pooling adhesion to snow
On snow		spreading adhesion to snow

tance (perhaps as much as 100 km), and as the ice melts to release the oil, oil is spread over a wide area. Spreading is also a factor that changes very much with ice conditions. Spreading on open water is slower with increasing ice coverage. Spreading on water covered with frazil or grease ice (new crystalline ice in a slush form) or brash ice (ice in chunks up to 2 meters in diameter) is very slow. Studies have been conducted on the spread of oil under ice, and models have been developed for this process. Oil will fill the cavities under ice and be swept along with the current. Studies have shown that spreading and transport by currents will spread oil very widely under ice. Oil spilled on top of ice surfaces will also spread, depending on ice roughness and snow cover. Snow will absorb the oil and retard its spreading. As this oil is heated by the sun, it quickly sinks below the snow/ice line and thus does not affect the bulk albedo for that area (Fingas, 2000).

Oil trapped under first-year ice will rise through the ice to the surface through brine channels during spring. The oil will form pools on the surface of the "rotting" ice and then enter the water as the ice completely melts. Oil trapped under multiyear ice will remain there until it rises through cracks. There are no brine channels in multiyear ice. If there are no cracks, the oil may rise through the natural ablation of ice over a multiyear period, perhaps 7 to 10 years. Less is known about the fate of oil under multiyear ice. Oil caught in leads (cracks in pack ice) may be forced under the ice as well or, if the lead closes rapidly, it can be forced to the ice surface. Often leads will freeze over and thus freeze the oil at the same time as would occur on open water.

The ultimate fate of oil in the Arctic depends largely on the location and ice conditions; however, the effect of the ice is generally to slow the spreading and contain the oil when it is first spilled, compared to open water conditions. Oil caught in ice and snow over winter will generally be released in spring when the ice melts. Adherence to snow and ice may ultimately result in widespread distribution of the oil in the spring or summer. Table 4-5 summarizes the fate of oil in an ice environment.

Fates of Subsurface Releases

Oil spills sometimes are not released at the surface but further down in the water column. Examples include natural seeps, blowouts during drilling of exploratory wells, pipeline leaks, and shipwrecks. Subsurface releases differ from surface releases in several important ways. First, oil can move substantial distances beneath the surface before it finally floats to the surface. This is especially true in deeper water where currents are strong. Such behavior makes tracking difficult, but more importantly it potentially provides time for the more soluble oil fractions to dissolve. Dissolution is enhanced because of mixing and higher pressure, and other aspects.

The special nature of subsurface spills was not been addressed in previous NRC (1975, 1985) reports. The latter report did discuss the Ixtoc spill, which was a subsurface spill, but it did not examine in any detail the subsurface nature of that spill. To facilitate this discussion, subsurface releases are separated into deepwater and shallow water, corresponding to a break at roughly 200 m. The separation is due to a number of physical and chemical complications that arise in deeper water.

Shallow-Water Releases

Considerable research has been conducted and measurements have been made on subsea shallow releases in the last 25 years. Initial efforts at modeling started with Topham (1975), followed by McDougall (1978), Fannelop and Sjoen (1980), and Milgram (1983). Through these efforts, the so-called integral plume models evolved based on an Eulerian reference frame. Zheng and Yapa (1998) and Yapa and Zheng (1997) improved the efficiency of the integral plume model using a Lagrangian scheme and incorporated more realistic ambient currents. Arguably their biggest contribution has been in verifying the integral plume model through extensive comparisons with analytical solutions and through laboratory and field experiments. Of most interest are their

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TABLE 4-5 Fate of Oil in Ice Environments

Location	Sublocation	Fate during freeze-up	Oil fate after thaw
On water	<3/10 ice cover	as open water	melt out onto open water
	>3/10 ice cover	largely trapped among ice	melt out onto open water
	In leads	frozen into leads or on edges	melt out onto open water
	With frazil.grease/brash ice	frozen into brash ice	melt out onto open water
Under ice	Under first year ice	encapsulated	rise through brine channels to surface
	Under multiyear ice	encapsulated	rise through cracks to surface or remains encapsulated
In ice	Encapsulated	remains encapsulated	melt out onto open water
On ice	On ice	will remain on ice	melt out onto open water
	Under snow	absorbed into snow	melt out onto open water
On snow		absorbed into snow	melt out onto open water

comparisons with two major field experiments conducted in 1995 and 1996 and described in Rye et al. (1996) and Rye and Brandvik (1997), respectively. The experiments released roughly 25 m^3 of oil in about 100 m of water in the North Sea. The Zheng and Yapas model compared well with the time it took the oil to reach the surface as well as the center location of the surface slick. However, no comparisons of hydrocarbon concentrations in the water outside the plume were made because of limited measurements in the field experiment.

The basic physics of a shallow-water release are as follows. If the oil or gas leaves the source under considerable pressure (i.e., blowout of an exploration well), there is a jet phase that consists of high-velocity fluid or gas (up to the order of 10 m/s) confined to a narrow but expanding cone. The initial momentum in the jet phase is dissipated rapidly within about 1 m of the release point. By this time, distinct droplets (and bubbles if gas is present) form with sizes that are a function of the details of the release but typically with a size distribution of the order of 3 mm (5 percent non-exceedence probability) although it can be much less in the case of very high exit velocities. Subsequently, the hydrocarbons start to rise as a "plume"—a collection of bubbles or droplets that act in concert to drag significant volumes of the adjacent sea water upward in the water column. Plumes rise at a different rate than individual bubbles or droplets, and this is accounted for in the existing models with a so-called slip velocity (the difference between the rise velocity of the mean bubbles or droplets and the plume). If gas is involved, the oil-gas plume will reach the surface in a matter of minutes driven by the large buoyancy of the gas bubbles. The resulting surface slick will spread into a thin film due to the radial outflow of entrained water near the surface. Radial velocities the same order of magnitude as the plume rise velocity (1 m/s) can be expected near the source (Milgram and Burgess, 1984). The typical film thickness will be in the order of 50-100 μm in slicks that are several kilometers wide. Initially, very heavy oil slicks can be as thick as 1mm or more. If the release consists of oil only, the rise time will be longer but still on the order of 10 minutes. If a substantial quantity of oil reaches the surface, spreading will occur, driven by gravity forces and restrained by surface tension and viscous forces in a manner similar to a surface slick.

If there is insufficient integrated buoyancy to set up the plume dynamics described above, the droplets or bubbles rise as individual elements at the rise velocity dictated by their diameter and shape. The threshold for plume dynamics is controlled largely by the volume of oil and gas released, and to a lesser degree, the details of the release orifice (which can control bubble and droplet size), the density of the fluids involved, and the ratio of oil to gas.

Strong cross-flowing currents can complicate the above picture in several ways. First, the plume will tend to bend over much as a plume of smoke is bent by the wind, resulting in a horizontal offset in the surfaced oil slick. Second, as identified initially by Hugi (1993), the rising bubbles or droplets can be sieved downstream according to size, with the largest bubbles rising on the upstream side of the plume and the smallest rising on the downstream side. If the cross-flow current is strong enough, the sieving process will disrupt the establishment of the plume, in which case the oil or bubbles will rise individually. Both these effects of cross-currents will influence how long the oil/gas takes to rise to the surface and where it surfaces. However, the differences in time are perhaps a factor of two and, in space, on the order of a hundred meters.

Another complication is that the oil droplets may entrain water and become emulsified much more quickly than they would in a surface release. Emulsification was observed at the Ixtoc blowout (Boehm and Fiest, 1982) and was due to the intense mixing and turbulence set up by this massive blowout. The presence of emulsified oil significantly impacts the weathering of the oil as discussed earlier. It also greatly lessens the buoyancy of the oil, thus increasing the time it takes for oil to reach the surface.

Deepwater Releases

Substantial efforts to study petroleum releases in deeper water have only recently begun, although there were a few

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early efforts—most notably studies of deepwater gas hydrate formation by Bishnoi and Maini (1979) and Topham (1984). Most recent efforts began in 1997 and were triggered by the expansion of hydrocarbon exploration efforts into deeper water. Results are starting to appear: Johansen (2000), Masutani and Adams (2000), Spaulding et al. (2000), Johansen et al. (2001), Chen and Yapa (2001), and Socolofsky and Adams (2001).

The present understanding of deepwater releases suggests they are much more complicated than those in shallow water. Figure 4-6 shows a schematic of the important processes, which are discussed in the subsections below along with some further comments on hydrates and overall hydrocarbon fates. Note that the water depth shown in Figure 4-6 is 1,500 m. In fact, all of the processes discussed below apply to water depths of 200 m or greater with the exception of hydrate formation.

Jet phase

This is the same as in the shallow water case except that there is potential for hydrate formation in deep water.

Plume phase

For most substantial releases, the discharged hydrocarbon will form a rising plume shortly after release, which is analogous to the previously described plume that forms in a shallow-water release. However, in deep water, the plume eventually entrains so much dense water that the aggregate density of the oil-gas-hydrate-seawater suspension is no longer buoyant. Once the plume sheds some of its heavier components, it may re-form as the plume ceases to rise, and "mushrooms." This process can occur numerous times (known as peeling). Whether or not a given plume reaches a terminal level will depend on the depth of discharge, the plume buoyancy (flow rate and composition of oil, gas, and hydrates), and the strength of the ambient stratification. Most substantial releases will reach a terminal depth within an order of 100 meters of the release orifice although it can be much higher especially if the stratification is weak.

As in the case of the shallow release, a crosscurrent may add the complication of bending and/or sieving (see earlier discussion of shallow releases), although the effect will be even stronger. Also, like the shallow-water case, there must be sufficient integrated buoyancy to set up a plume. If the volume is too small or the bubbles or droplets are too small, then the plume is not established and movement will look like the post-terminal phase described below.

Post-terminal phase

Once the plume reaches its final terminal layer the rise of the oil-gas-hydrates is driven purely by the balance between the buoyancy of the individual droplets, bubbles, and hydrate flakes, and their hydrodynamic drag.

Hydrates

Natural gas released deeper than about 300 m can theoretically form hydrates based on thermodynamic equilibrium calculations. However, the recent laboratory and experimental studies cited above suggest that these calculations predict hydrate formation prematurely. For example, in a field experiment, Johansen et al. (2001) found that the thermodynamic equilibrium suggested for hydrate formation should have occurred below 450 m, but no hydrate was observed at the release depth of 840 m. The laboratory experiments of Masutani and Adams (2000) suggest that hydrate formation requires saturation of the water with the gas.

Hydrate formation is an important factor in determining how quickly oil rises to the surface. Hydrate has a specific

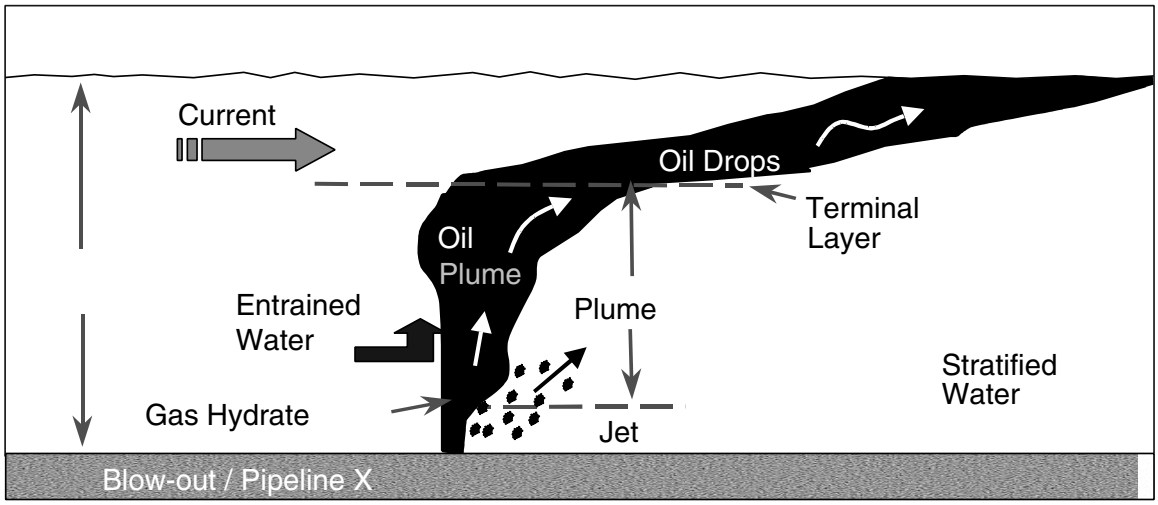

FIGURE 4-6 Schematic diagram depicting the basic physical processes involved in a deepwater subsurface oil and gas release.

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gravity of roughly 0.9, so if it forms, much of the buoyancy driver disappears from the plume, thus increasing the time it takes the hydrocarbon to reach the surface.

At some very great depths or very high volumes of gas release, hydrates will form. As the hydrate rises above the critical depth it will start to decompose. If it is a flake, it will decompose into small bubbles that will almost certainly dissolve in the water before reaching this surface. If the hydrate consists of a thin skin as observed by Masutani and Adams (2000), then the skin will decompose and the bubble dissolve.

Deepwater release fates

Based on the work cited above, several important aspects of the fates of deepwater releases have become apparent:

- The majority of the oil in most deepwater releases will rise to the surface although it may take several hours. Theoretical calculations of a light-weight oil suggests that, at most, 10 percent might dissolve under perfect conditions. For a diesel and a light medium crude, Johansen et al. (2001) found that it took about an hour for hydrocarbons to appear at the surface when released from 800 m of water.
- The surface slick formed once the oil reaches the surface will be thinner than that seen during a shallow-water release or a surface release. This is due in part to the fractionation of oil droplets that results in a staged arrival of the oil at the surface and in part to diffusion or dispersion of the oil as it rises.
- Much if not all of the natural gas (85 percent methane or more) associated with the oil will likely be dissolved in the water column, regardless of whether hydrate forms or not. This is due to the high solubility of methane in sea water at the high pressures and cold temperatures found in deeper water.
- Integral plume models like those of Johansen (2000) and Chen and Yapa (2001) do appear to capture much of the major features observed in the field including the terminal layer and time to surface.

Despite the fact that surface slicks capture the public attention, there are a substantial percentage of accidental spills that occur beneath the surface, typically from the seafloor. Examples include blowouts of exploration wells, pipeline ruptures, and shipwrecks.

The release of oil beneath the surface introduces a number of complications compared to oil released at the surface. From the standpoint of fate the most important complications are enhanced dissolution in the water column and, perhaps, emulsification. If natural gas is present it will tend to dissolve rapidly during the rise through the water column.

The state of modeling is well advanced in shallow water in many respects. Several integral plume models compare well to field data, which include the time the oil takes to reach the surface, the size and shape of the rising plume, and the surface slick. In deeper water, the models are just now appearing. Predicting hydrate formation and emulsification appears to be problematic. The most serious, in terms of fate problems, for both shallow and deepwater appears to be the limited validation of the dissolved component. Without this, it is difficult to assess some potentially important fates.

MODELS AND MODELING

Conceptual Model

In order to better understand the interplay of the various processes discussed earlier, it may be worthwhile to examine the potential fate of a petroleum spill through the development of a conceptual model. (A conceptual model in this sense, is not a software application, but a conceptual tool that might lead to the development of a computer model or, more likely, a group of models—many of which are already available.) A conceptual model for the fate of oil in the environment should start with the most basic sources of crude oil. The model should then trace the products and by-products of oil refining and their ultimate fate in the environment. That is, the model should perform a mass balance on the oil beginning with its extraction from below the surface to its ultimate receptor (e.g., sediment, animal tissue, atmospheric gas). In this case the basic sources would be:

- natural seeps
- land-based oil production facilities
- offshore platforms

The conceptual model should then trace the transport and fate of this material as it moves from source => refinery => use => recycling => waste => environment. For the present study, whose the emphasis is on the *fate* of oil and its by-products in the marine environment and the subsequent *effects* on biota, only inputs of petroleum hydrocarbons to the marine environment in time and space have to be taken into account. The fate of these inputs is tracked using three-dimensional transport and weathering models within the water column, the sediments, and the biota. Figure 4-1 illustrates this conceptual model, which partitions the marine environment into three interdependent environmental compartments or modules—the water column, bottom sediments, and biota. The various mechanisms whereby petroleum hydrocarbons move from one module to another are identified on the figure. Petroleum hydrocarbons are introduced into either the water column or the bottom sediments from one or more of the external sources shown in the rectangular boxes. Describing the *fate* of petroleum hydrocarbons in the ocean requires tracking their movement from the external source through each environmental compartment. The *effects* of oil in the sea are described in the bottom sediments and biota modules. The approach to developing a quantitative expression of the fate and/or effects within each of the modules is discussed below.

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External Sources

The conceptual model is driven by external sources of petroleum hydrocarbons as shown on Figure 4-1, including:

- atmosphere
- coastal runoff
- rivers
- spills
- operational discharges
- seeps

In Chapter 3 of this report, each of these sources is quantified by coastal zone within North America. To quantitatively describe the fate and effects of these external sources, they must be redefined as *point* sources or diffuse sources, and then further quantified in time and space. The division of the external sources into point and diffuse sources can be done as follows:

1. Point sources:
   - Spills (vessels, platforms, pipelines, facilities)
   - Rivers
   - Produced water
   - Coastal refinery wastewater
2. Diffuse sources:
   - Natural seeps
   - Atmosphere on open seas
   - Coastal urban runoff
   - Marine transport operations
   - Recreational boating

The time and space scales required to characterize these inputs depend on the degree of time and space definition desired for examining fate and effects. For example, to track the fate and effects of a medium-sized spill where the initial concern is toxic effects and physical adsorption on animals, the time scale would be on the order of days and the space scale meters. Each of the environmental modules (with the possible exception of bottom sediments) would also have to describe fates and effects within the compartment in similar time and space scales until the short-term effects of the spill were no longer discernible. Then the long-term effects of the spill might be calculated at seasonal time steps, with space scales in kilometers.

For minor spills that occur frequently in a geographic area, the effects of these discharges would most likely exhibit themselves as chronic effects. Thus, these minor spills could be categorized as diffuse sources, constant in time (or season) and space over a specified geographic area.

Most of the other inputs can be considered constant in time (or seasonal), and fixed in space. Time scales for the environmental compartments can thus be seasonal, with space scales in kilometers.

Transfer of Materials Within and Between Modules

Within each module, equations governing the processes that occur in the module can be developed to whatever extent is desirable, (i.e., simple models to complex models; single compound models to multiple-compound models). Most likely, a single physical oceanographic circulation model could be used as the basis for the transport calculations performed in the water column and the bottom sediments. The macro biological part of the biotic module is the ultimate system of interest in terms of effects, and the other two modules are required only to the extent necessary to accurately define the transfer paths between them and the biotic module.This model is probably good for all animals, including birds with respect to oil impacts due to ingestion, but it is not suitable for physical effects such as coating of the animals with oil, which has occurred during significant oil spills. The approach to quantitatively describing the fate and effect processes that occur in each environmental module is discussed further below.

The Water-Column Module

The water-column module does not describe any *effects* of oil in the ocean, but rather describes the *fate* of petroleum hydrocarbon compounds within the water column. The processes include interrelating transfers to and from the water column from external sources and the other two environmental modules and calculating internal biochemical transformations of petroleum hydrocarbon compounds (weathering). The water-column fate model can be expressed using a mass-balance model in the form of differential equations.

The Bottom-Sediment Module

The bottom sediments module shown on Figure 4-1 is also a *fates* module describing (1) chemical weathering of petroleum hydrocarbons within the sediment, (2) the transfer across the sediment-water interface of petroleum hydrocarbon compounds between the sediment module and the water column, and (3) transfers of petroleum hydrocarbon compounds between the sediment and biota modules by benthic organisms. It would be possible to include the benthic organisms in the sediment module, but it is conceptually easier to have the biological process confined to one module (the biota module). A simple two-dimensional (horizontal) mass-balance model can be written for the sediment module and also can be put in the form of a differential equation. More complex models can be envisioned involving, for example, aerobic and anaerobic processes that take place in the sediment and also, the water column.

Note that *transport* is included on Figure 4-1 in the bottom-sediment module. Transport of bottom sediment would occur in river deltas during times of high flow (such as seasonal high flows or flood flows) or anywhere in the intertidal

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zone due to episodic events such as upwelling or hurricanes. Quantifying this phenomenon would be very difficult and most likely would not result in any increase in the accuracy of tracing the fate and effects of oil in the ocean.

The Biota Module

The biota module is the most difficult of the modules to describe quantitatively. It includes both fates and effects. To better illustrate the processes that must be quantified in this complex module, the biota module shown in Figure 4-1 is illustrated in more detail in Figure 4-7.

Basically the fate of petroleum hydrocarbons in the biota module results from (1) ingestion (uptake) of one suite of petroleum hydrocarbons by an organism and subsequent excretion to the sediment or the water column of a different suite after digestion and metabolism; (2) transfer of petroleum hydrocarbons up the food chain through the predator-prey relationship; and (3) sorption or ingestion of petroleum hydrocarbons by a marine organism followed by death of the organism and return of the petroleum hydrocarbon to the water column or sediment column through biochemical decay of the organism. In addition, certain petroleum hydrocarbons will be carried away from the sea by birds, and land-based animals, when oil adsorbs on their bodies and they carry the oil away from the sea or ingest seafood and then excrete products or die onshore.

Perhaps the best way to quantitatively describe the biota module would be through the application of a trophic-level food web model that describes the movement up the food chain of petroleum hydrocarbons ingested at any given level. Writing an ingestion-growth-excretion relationship for each trophic level and coupling trophic levels with a predator-prey relationship would enable one to track the migration of petroleum hydrocarbons through the food chain and to determine the concentration of the petroleum hydrocarbons per gram of biomass at each trophic level. Ingestion into the food chain would be a sink for petroleum hydrocarbons in the water-column or bottom-sediment modules, and petroleum hydrocarbons excreted in the biota module would become sources for the water-column or bottom-sediment modules.

Computer Models

The advent of fast personal computers has enabled the development and wide distribution of a number of fairly comprehensive composite fates models that include many of the elements in the ideal conceptual model described in the pre-

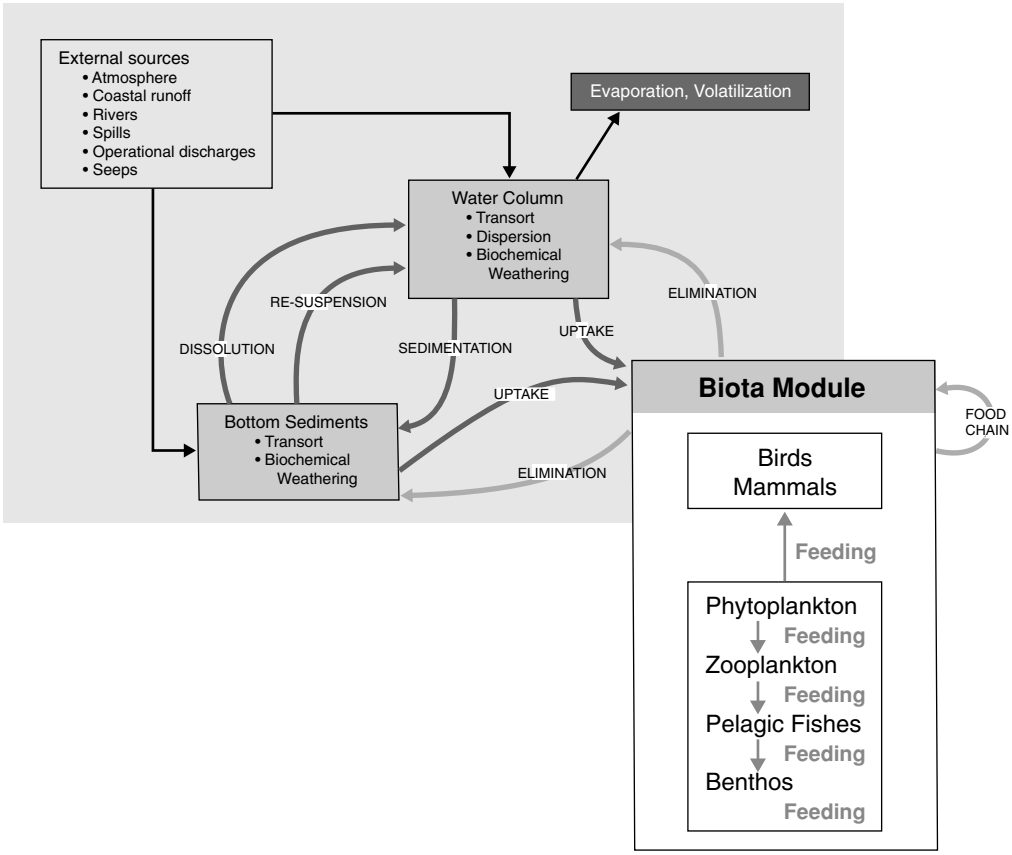

FIGURE 4-7 Detailed interactions among components of the biota module of conceptual model for the fate of petroleum in the marine environment shown in Figure 4-1.

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vious section. Most of the models have focused largely on surface oil slicks. Several of these models have graphical user interfaces and integrated Geographical Information Systems (GIS) and are widely used by agencies and industry for:

- **Tactical (emergency) spill response.** In the event of an accidental spill, a composite model is often used to predict where the spill will go and how it will weather. This kind of information plays a key role in determining protection priorities.
- **Strategic (contingency) planning.** The models are run in a stochastic manner (multiple-runs) to develop maps of the probability a spill would impact a region given that a spill occurs.
- **Post-Spill assessment.** The models are used after a spill to fill observation gaps and estimate damage. Another use is to determine the source of unknown oil. In this model, one knows where the spill ended up but needs to determine the most likely origin to identify the responsible party.

There have been two reviews of composite oil slick models published recently: ASCE (1996) and Reed et al. (1999). ASCE (1996) cites more than 50 composite slick models in existence at the time of its study. Clearly a complete review of all these models would be a major publication in itself and is beyond the scope of this report. Nevertheless a closer look at a few representative models does provide valuable insight into the present state of the art. Table 4-6 summarizes and differentiates among four widely used composite models. Some of the differences in Table 4-6 are a result of the fact that the models are intended for different purposes. SIMAP is primarily for strategic planning and perhaps post-spill assessment. OSIS and GNOME/ADIOS2 can be used for all three purposes: tactical planning, strategic planning, and post-spill assessment. OSRA is focused on strategic planning. The intent of Table 4-6 is to provide an overview of the range of models. The rows in the table indicate how each model accounts for the major processes identified in the previous sections. Two of the models are used by U.S. government agencies, while the other two are commercially available and widely used by private industry.

The National Oceanic and Atmospheric Administration has a primary responsibility in providing spill modeling expertise to the U.S. Coast Guard during major spills in U.S. waters. NOAA also works in other parts of the world on an invitation basis. NOAA actually uses two models: GNOME to account for advection, spreading, and first-order evaporation and ADIOS2 to estimate detailed weathering, dispersion, and so forth. The Minerals Management Service (MMS) model known as OSRA (Smith et al., 1982) is used to estimate spill impact probability associated with offshore oil development in the Outer Continental Shelf (OCS). This model is a key consideration in determining the potential environmental impact of future oil and gas developments. OSIS (Leech et al., 1993) is a commercial product frequently used in Europe. SIMAP (French, 1998) is another commercial product that is used in the United States especially for post-spill Natural Resources Damage Assessments

TABLE 4-6 Summary of Processes Included in Four Composite Models

Process	GNOME-ADIOS2 (NOAA)	OSIS (BMT)	OSRA (MMS)	SIMAP (ASA)
Dimensions	Near-surface	Near-surface	Near-surface	Entire water column
Advection	Wind factor + background + stochastic uncertainty	Wind factor + background current + wave (Elliot and Wallace, 1989)	Wind factor + background	External hydrodynamic model + wind factor (if not in hydro model)
Horizontal dispersion	Fickian	Random walk based by Morales et al. (1997)	Optional	Heuristic method + spillets
Spreading	Modified Fay + wind component	None	None	Modified Mackay et al. (1980)
Emulsification	Eley (1988)	Mackay et al. (1980)	None	Mackay et al. (1982)
Vertical dispersion (entrainment)	Modified Delvigne and Sweeney (1988). Includes wave break and Langmuirs	CONCAWE (Van Oudenhaven et al., 1983)	None	Delvigne and Sweeney (1988)
Dissolution	None	None	None	Mackay and Leinonen (1977)
Evaporation	Modified Payne (Jones, 1997)	Stiver and Mackay (1984)	None	Stiver and Mackay (1984)
Oxidation	None	None	None	First order decay with heuristic components
Sediment & settling	Payne (1987)	None	None	French et al. (1999)
Subsurface release	None	None	None	Simple passive point source
Coastal-interaction	All oil sticks	All oil sticks	All oil sticks	COZOIL (Reed and Gundlach, 1989)

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(NRDAs). SIMAP calculates effects as well as fates, but only the fates component is discussed here. OilMap is a widely used relative of SIMAP that considers only near-surface fates, but does provide a choice of process algorithms. As indicated in Table 4-6, three of the four models consider only surface waters. SIMAP is apparently the only widely available model that considers the entire water column. In addition it tracks four oil components separately:

- monoaromatics: aromatics with molecular weights (MW) less than 100 g/mole;
- polynuclear aromatic hydrocarbons (PAH): volatile aromatics with MW between 100 and 200 grams/mole;
- non-aromatic volatiles (<200 g/mole MW); and
- a residual fraction that is neither volatile nor soluble (>200 g/mole MW).

A comparison between SIMAP and the Conceptual Model of Figure 4-1 shows that SIMAP accounts for all the processes, although obviously each process submodel is often far less than ideal. The simplest model in Table 4-6 is the OSRA model, although it is more complex than can be described in a table. A multiple-step process is actually involved. The first step is to run the basic OSRA model in a Monte Carlo fashion to establish contact probability and time-to-impact contour maps. The second step is to look at weathering and dispersion of some specific spill scenarios impacting critical resources. The first step gives the probability that the spill will hit that resource along with the time to impact. Weathering for these specific scenarios is calculated using NOAA's ADIOS2, described in part in Table 4-6.

Composite models compare reasonably well with observations. ASCE (1996) briefly compares hindcast results from several two-dimensional models with data from two actual spills (simulations for three historical spills are given, but observations are included for just two of the three). The focus is on time periods on the order of one week after a sudden surface point source spill, with observations consisting of time series locations of major patches of oil. (Comparisons are only for surface oil. No modeling was attempted for overwashed oil.) In general, the ASCE (1996) study concluded that the models evaluated did well, but also noted several major limitations should be kept in mind:

- The comparisons are largely qualitative, and no mass-balance comparisons are possible because of the lack of comprehensive field observations.
- The models are run in "hindcast" mode, i.e., after the fact. Actual wind and especially current measurements are minimal; thus the current and wind inputs into the model are modified so that the modeled slicks track the observed one as closely as possible.
- If the models are run in a "forecast" mode in which future winds and currents must be estimated, then model forecasts will often deviate substantially from observations.

The cases considered by ASCE (1996) are quite limited in the context of the greater problem of "Oil in the Sea." For example, these cases did not consider subsurface releases, continuous point sources, non-point source releases, or long-term (greater than one week) fates (for more details see ASCE [1996]). French (1998) provided some comparisons between fates and effects calculated from SIMAP, as observed during the *North Cape* oil spill. Comparisons were generally good.

FATE OF OIL INPUT

Table 4-7 is a summary of the fate processes that affect petroleum hydrocarbons from the seven major input categories. Each input is ranked using a scale of high, medium, and low that indicates the relative importance of each fate process. Table 4-7 was developed by consensus of the committee and is based on many assumptions. It is intended to provide only a general idea of the relative importance of the fates processes. Clearly one of the biggest problems in developing a table such as this is that the importance of a particular fate process will depend on the details of the event. The committee has tried to account for this to a limited extent in the case of accidental spills by including subcategories for various oil types. With these caveats in mind, an explanation of each of the fates is as follows.

Evaporation-volatilization is ranked according to the relative volume of the release that would be lost by net transport from the sea surface to the atmosphere. For example, gasoline would have "high" evaporation whereas a heavy crude would be "low." Evaporation has been ranked "high" for two-stroke engine inputs, which consist largely of unburned gasoline. Emulsification rankings are driven largely by the oil type whereby gasoline, which has no emulsification potential, would have a low ranking, while a medium, fresh-crude could have a high ranking, although this depends on the specific crude composition.

Dissolution rankings consider the total water-soluble fraction, the rate of dissolution, and the rate of volatilization from the water, reflecting the relative potential of releases to impact water-column resources.

Oxidation rankings reflect the relative rate and extent of oil removal by microbial and photooxidative degradation for those oils that have moderate persistence in the marine environment. Thus, releases of crude oils are ranked "medium" because microbial degradation is a significant weathering process for the intermediate-weight hydrocarbon components in crude oil, whereas releases of heavy, weathered oils are ranked "low" because they are recalcitrant to microbial and photodegradation. In contrast, light oils such as gasoline and light distillates are mostly lost by evaporation-volatilization (Figure 4-2) and not to oxidation, and are ranked as not relevant.

Horizontal transport is a combination of spreading, advection, and horizontal dispersion, and the rankings are

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TABLE 4-7 Processes that Move Petroleum Hydrocarbons Away from Point of Origin

	Weathering									
Input Type	Petroleum Persistence	Evaporation	Emulsification	Dissolution	Oxidation	Horizontal Transport or Movement	Vertical Transport or Movement	Sedimentation	Shoreline Stranding	Tarballs
Seeps	years	H	M	M	M	H	M	M	H	H
Spills										
Gasoline	days	H	NR	M	L	L	L	NR	NR	NR
Light distillates	days	M	L / L	H	L	M	H	L	L	NR
Crudes	months	M	M	M	M	M	M	M	H	M
Heavy distillates	years	L	M	L	L	H	L	H	H	H
Produced water	days	M	NR	M	M	L	L	L	L	NR
Vessel operational	months	M	L	M	L	M	L	L	L	M
2-stroke engines (gasoline & light distillates)	days	H	NR	M	L	L	L	L/NR	NR	NR
Atmospheric	days	H	NR	M	M	H	NR / NR	L	NR	NR
Land based	U	M	L	L	L	M	M	M	NR	U

NOTE: H = high; L = low; M = moderate; NR = not relevant; U = unknown

driven by the persistence of the release on the water surface as well as the areal extent of the input. Thus, even though atmospheric inputs are expected to have low persistence because they volatilize quickly, they are introduced over large areas compared to point sources such as spills. Heavy oils and seeps form residues that can persist at sea for long periods.

Vertical transport and movement include the processes of vertical dispersion, entrainment, Langmuir circulation, sinking, and overwashing. Rankings reflect the potential for mixing into the water column by natural processes, given that very light oils evaporate quickly and heavy oils are too viscous to disperse naturally. Sedimentation rankings consider the suspended sediment concentrations at the release sites and the potential for the oil to adhere to sediments after stranding onshore or by mixing with suspended sediments.

Shoreline stranding is ranked highest for those petroleum hydrocarbons that persist on the water surface and are likely to be released close to shore, increasing the potential for a significant amount of the released oil to strand. Tarball formation, like shoreline stranding, is ranked highest for releases of crudes and heavy oils that form persistent residues.

Seeps

Crude oil released into the marine environment through natural seepage undergoes most of the same physical and chemical process as crude oil released into the ocean at the seafloor. One main difference is in the rate of addition of oil to the environment. With natural oil seeps, the leakage rate is relatively low and chronic. On the other hand, oil spills result in a release that is a sudden, one-time event. The same basic processes act to degrade and remove oil with time, although in the case of seeps, crude oil is replenished as long as the seeps remain active. Thus, the persistence of natural oil seeps is reckoned in terms of years.

Ranking the fate processes that move petroleum hydrocarbons away from natural oil seeps is difficult because these seeps occur worldwide in numerous geographic settings. In the four major weathering processes of evaporation, emulsification, dissolution, and oxidation, they are ranked "medium." The overall ranking is similar to that of crude oil spills. Also, comparison between natural seeps and crude oil spills show the similarities in rankings between the processes of transport, sedimentation, shoreline stranding, and tarball formation.

Spills

Spills range widely in oil type, spill size, location, and environmental conditions during the release.

Gasoline

With a very low viscosity, gasoline spills spread rapidly as thin sheens. Gasoline is also light, with a specific gravity of about 0.8, so it causes a slick on the sea surface, or rapidly re-floats if dispersed into the water column. Evaporation-volatilization is the dominant process affecting spills on the water surface and may eliminate nearly all of the spilled gasoline within a few hours to a day. As a result, gasoline spills in marine waters have low persistence. There is little potential for spreading, mixing into the water column, sedimentation, or stranding, and no risk of forming emulsions or

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tarballs. Even though gasoline has the highest water solubility of all oil types, dissolved concentrations under slicks decrease rapidly by evaporation.

Light Distillates

Light refined products, such as diesel, No. 2 fuel oil, jet fuels, and kerosene, are narrow-cut fractions that have low viscosity and spread rapidly into thin sheens. They do not tend to form emulsions except under very cold conditions. They evaporate more slowly (compared to gasoline) and incompletely; therefore, they are ranked as "medium" in terms of their horizontal transport or movement. As low-viscosity, moderately persistent oils, light distillates tend to disperse readily into the water column by even gentle wave action. Thus, they have the highest potential of any oil type for vertical mixing. There is also a greater potential for dissolution to occur, from both surface sheens and droplets dispersed in the water column. The water-soluble fractions are dominated by two- and three-ringed PAH, which are moderately volatile and may affect aquatic biology. Thus, spills of light distillates have the greatest risk of impacting water-column resources. Light distillates are not very adhesive; therefore, they do not adhere strongly to sediments or shoreline habitats. Loading levels on the shoreline are relatively low because of the thinness of sheens on the water surface and the low adhesion of stranded oil. The constituents of these oils are light to intermediate in molecular weight and can be readily degraded by aerobic microbial oxidation. Long-term persistence in sediments is greatest under heavy loading and reducing conditions where biodegradation rates for anaerobic bacteria are low.

Crude Oils

Crude oils contain a wide range of compounds, from light to heavy; thus, they are affected by many fate processes. Evaporation can remove about one-third of the volume of a medium crude oil slick within the first day, but there will always be a significant residue. Many crudes will emulsify readily, a process that greatly reduces subsequent weathering rates. As a result, crude oil spills close to shore often strand and persist on shorelines, particularly on permeable substrates such as gravel beaches and sheltered habitats such as marshes. Crude oils tend to adsorb heavily onto intertidal sediments, with the risk of subsequent erosion of oiled sediments from the shoreline and deposition in nearshore habitats. Under high-energy, nearshore conditions, oil and sediments can mix and be transported to the bottom sediments. For spills that are transported offshore, the slicks eventually break up into fields of tarballs that can be transported long distances because they are so persistent. The water-soluble fraction of crude oils include a wide range of PAH. Dissolution from slicks and stranded oil can persist for weeks to years.

Heavy Distillates

These oil types, such as No. 6 fuel oil, bunker C, and heavy slurry oils, lose only up to 10 percent of their volume via evaporation. Some products are so viscous that they cannot form emulsions, but many emulsify shortly after release. They show low natural dispersion because the oil is too viscous to break into droplets. These oils have the lowest water-soluble fraction; thus, loadings to the water column are generally low under slicks. Spills of heavy distillate quickly break up into thick streamers and then fields of tarballs that are highly persistent. The heavy distillate can be transported hundreds of miles, eventually stranding on shorelines and posing significant impacts to birds and other marine animals such as turtles. Because of their high density, these releases are more likely to sink after picking up sediment, either by mixing with sand in the surf zone or after stranding on sandy shorelines. Some heavy distillates are so dense that they are heavier than brackish or sea water and will not float when spilled.

Produced Water

Large volumes of produced water are discharged in offshore oil-producing areas. Produced water is treated to remove most free oil prior to discharge; however, the water still contains a moderate amount of soluble and volatile petroleum hydrocarbons. The concentrations of benzene, toluene, ethylene and xylenes (BTEX) in produced water vary by almost a factor of 10, with an average concentration of about 5 mg/L. The polynuclear aromatic hydrocarbons (PAH) also vary by about an order of magnitude, with an average concentration of about 1 mg/L. Because these compounds are already in solution, their concentrations are reduced rapidly by volatilization and dilution, particularly when released to open, well-mixed waters. Elevated levels of contaminants in sediments typically extend 100-200 m from the discharge point. There are occasional events in the treatment process that result in light sheens, but they are expected to disperse rapidly with a low risk of stranding on shorelines and no risk of emulsification or tarball formation.

Vessel Operational Discharges

Operational discharges from vessels generally occur more than 50 miles from shore and are concentrated along shipping lanes. Discharges are composed of bilge water, cargo tank washings, fuel oil sludge, and other oily wastes, which are all considered moderate in terms of their loss by evaporation and dissolution, formation of tarballs, and potential for long-distance transport. Vessel discharges pose a low risk of vertical mixing because the releases are generally viscous. Because these discharges are released in offshore waters, there is low potential for contact with sediments and sedi-

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mentation, and shoreline stranding is a concern only where shipping lanes pass close to shore.

Recreational Marine Vessels

Fuel for two-stroke outboard engines is a mixture of gasoline and lube oil in volume ratios varying from 20:1 (5 percent) in older engines to 50:1 (2 percent) in newer models. The bulk of the fuel, gasoline, is comprised of the lighter, molecular-weight fraction (e.g., BTEX) and volatilizes from the surface water. The rate of volatilization is temperature dependent, but the product will remain for several minutes to hours at 15°C, given the amount of gasoline that is emitted from two-stroke engines in coastal waters and the time of year that they are used (usually during warm periods, when biological productivity is highest). The potential effect from toxins, such as PAH, in unburned gasoline and lubricating oil, on the biota including larvae and phytoplankton is large (see Chapter 5 for greater discussion of potential environmental effects from the release of refined petroleum products). To date there are no published field studies evaluating the effect of gasoline released from the operation of two-stroke engines.

The lube oil mixed with gasoline forms the sheens and slicks that trail behind two-stroke engines during operation. Evaporation and dissolution are the most important fate mechanisms. After two days, nearly 75 percent of the lubricating oil can evaporate at 15°C (Figure 4-2). A smaller portion of the light lube oil can remain on the surface marine microlayer for longer periods (days) depending on environmental conditions including physical, chemical, and biological processes.

Land-based Sources

Unlike the discharge of liquid petroleum, hydrocarbons that enter the coastal ocean from land-based sources via rivers have already undergone considerable biogeochemical weathering. Land-based sources result from petroleum inputs to streams and rivers and subsequent transport to surface coastal waters. This transport is selective, with more water-soluble and stable components of the petroleum mixture carried downstream. During riverine transport, the petroleum mixture can undergo further weathering, including evaporation-volatilization and microbial degradation, such that the material reaching the coastal ocean is likely more stable and recalcitrant than the original mixture.

In addition to weathering between the release point and the coastal ocean, the nature of the river transport will play a major role in the magnitude and fate of petroleum products reaching the ocean. A good example is the differential behavior of petroleum transport in the Columbia River and the Chesapeake Bay. The Columbia is a large, relatively fast-flowing river whose plume discharges directly into the coastal Pacific. Petroleum hydrocarbons entering the Columbia River are likely transported rapidly to the coastal ocean, with relatively little retention within the river basin. The Chesapeake Bay, on the other hand, is a shallow, productive, semi-enclosed estuary with a long water residence time and a well-characterized ability to trap eroded solids. Due to its large surface area-to-volume ratio and its relatively high sedimentation rates, the Chesapeake Bay is likely to efficiently transport petroleum hydrocarbons entering from the tributaries. While this trapping reduces the loadings of petroleum hydrocarbons to the coastal oceans, it may result in locally enriched hydrocarbon levels in estuaries and other embayments. (Note that in this report, tidal embayments are included as part of the coastal ocean, so these removal processes in estuaries would be counted as "losses" from the coastal ocean.)

Atmospheric Deposition

Petroleum hydrocarbons enter the coastal ocean from the atmosphere by wet deposition (scavenging of atmospheric hydrocarbons by precipitation), dry aerosol deposition (transport of marine aerosol particles to the sea surface), and gas exchange. Of these three, it is estimated that gas exchange dominates the total gross loading of hydrocarbons from the atmosphere. Since gas exchange results from the dissolution of gaseous hydrocarbons in sea water, the magnitude of its flux depends on the concentration in the gas phase and the solubility of the hydrocarbon in sea water. Unlike the other sources discussed in this report, atmospheric deposition supplies hydrocarbons somewhat uniformly to the coastal ocean at relatively low loading rates over large areas.

Analysis of the concentrations of petroleum hydrocarbons in the coastal ocean indicates that the surface waters are greatly oversaturated with *n*-alkanes with respect to the overlying atmosphere. All of the input sources discussed in this report lead in varying degrees to these ambient concentrations in the coastal ocean. Volatilization is the dominant fate process for petroleum hydrocarbons. Terrestrial hydrocarbon loadings (land-based sources) and other nearshore sources support dissolved hydrocarbon loadings in coastal waters that far exceed the loadings in equilibrium with the atmosphere. Hydrocarbon degassing to the atmosphere from coastal water is therefore a major geochemical process.

Summary

The behavior and fate of crude oil and refined products in the marine environment are controlled by many different processes that vary considerably in space and time. Physical, chemical, and biological processes all interact to (1) alter oil introduced into the oceans; (2) transport the resulting degradation (weathering) products away from the source; and (3) incorporate the residual substances into compartments of the earth's surface system. These compartments involve disso-

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PHOTO 18 Refinery capacity is an important factor in gasoline prices. However, such facilities are also sources of petroleum spills and atmospheric releases of volatile organic compounds that can play a role in local air quality. In the United States most refineries are located near marine transportation terminals along the Gulf of Mexico and the northeastern Atlantic seaboard. (Photo courtesy of Environmental Research Consulting.)

lution in the hydrosphere, deposition in the lithosphere, volatilization into the atmosphere, and ingestion by organisms in the biosphere. Physical processes degrading oil include evaporation, emulsification, and dissolution, whereas chemical processes focus on photooxidation and biological processes emphasize microbial oxidation.

The transportation of oil in the marine environment occurs in two directions, horizontal and vertical. Horizontal transport involves spreading and surface advection, leading in some instances to shoreline stranding and tarball formation. Transport in the vertical direction includes dispersion, entrainment, Langmuir circulation, sinking, overwashing, and sedimentation. Consideration is also given to oil in icy conditions and oil released in deep water.

Conceptual models can be developed to build deterministic models for specific oil loadings for specific sources. The development and distribution of composite fate models, up to now, focus largely on surface oil slicks.

Oil entering the marine environment comes from natural sources (oil seeps) and from sources over which humankind has some control (oil spills, urban runoff, pollution resulting from oil transportation and production, and oil usage in ve-

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hicles, including boats). The ultimate fates of oil in the sea depend on the amount and rate of discharge, composition, source, and environmental setting and persistence.

The effect of petroleum hydrocarbon is not directly related to the volume released. It is instead a complex function of the rate of release, the nature of the released hydrocarbon, and the local physical and biological ecosystem. Some progress has been made in understanding the basic processes affecting fates such as evaporation. Much more needs to be learned about oil-sediment interaction, vertical dispersion and entrainment, dissolution, Langmuir cells, and hydrate formation (as related to deep subsurface releases of gas). Furthermore, the priorities for research into petroleum hydrocarbon fate and transport have historically been driven by large spills. Thus, resource allocation to support these efforts tends to wane in periods during which a large spill has not recently occurred. **Federal agencies, especially NOAA, MMS, the U.S. Coast Guard, and the USGS, should work with industry to develop and support a systematic and sustained research effort to further basic understanding of the processes that govern the fate and transport of petroleum hydrocarbons released into the marine environment from a variety of sources (not just spills).**

Response plans depend heavily on site-specific modeling predictions of the behavior of spills of various sizes and types, under a variety of environmental conditions. There is a need for both better baseline data, including ambient background levels of hydrocarbons in the sea, and better data for calibrating fate and behavior models. Because experimental release of petroleum is not feasible under most circumstances, comprehensive data on the fate of the oil must be collected during spills. Such efforts are generally neglected, because moving needed equipment and personnel to spill sites to collect data naturally is of lower priority than containing the spill and minimizing damage to the environment and property. **Federal agencies, especially the U.S. Coast Guard, NOAA, and EPA should work with industry to develop a more comprehensive database of environmental information and ambient hydrocarbon levels, and should develop and implement a rapid response system to collect in situ information about spill behavior and impacts.**

Natural seep systems and sites of historical spills offer good opportunities for field studies of the fate and effect of the release of crude oil and (in the case of spills) refined products, especially to understand dissolution and long-term weathering. **Federal agencies, especially the USGS, NOAA, EPA, and MMS, should develop and support targeted research into the fate and behavior of hydrocarbons released to the environment naturally through seeps or past spills.**

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5

Biological Effects of Oil Releases

HIGHLIGHTS

This chapter focuses on:

- The complexity of determining effects of petroleum hydrocarbons in the marine environment within the background of highly complex natural variables.
- The advances in our understanding of acute and chronic effects of petroleum hydrocarbons in the marine environment made since the 1985 NRC Review *Oil in the Sea*.
- The advances in modeling for assessing oil impacts in the marine environment.
- The advances in our understanding of how communities respond to petroleum discharges especially biogenically structured communities.
- The unique aspects of production fields and natural seeps in understanding the long-term effects of petroleum discharges in the marine environment.
- The identification of important information gaps that still exist in our understanding of the effects of petroleum hydrocarbons on populations of marine organisms and ecosystems and the time course of recovery.

Oil in the sea from anthropogenic sources, whether from spills or chronic releases, is perceived as a major environmental problem. Major oil spills occur occasionally and receive considerable public attention because of the obvious attendant environmental damage, including oil-coated shorelines and dead or moribund wildlife, especially oiled seabirds and marine mammals. Acute effects may be of short duration and limited impact, or they may have long-term population- or community-level impacts depending on the timing and duration of the spill and the numbers and types of organisms affected. Oil also enters the sea when small amounts are released over long periods, thus creating chronic exposure of organisms to oil and its component chemical species. Sources of chronic exposures include point sources, such as natural seeps, leaking pipelines, offshore production discharges, and non-point runoff from land-based facilities. In these cases, there may be a strong gradient from a high to a low oil concentration as a function of distance from the source. In other cases, such as with land-based runoff and atmospheric inputs, the origin of the oil is a nonpoint source, and environmental concentration gradients of oil compounds may be weak. Chronic exposures may also result from the incorporation of spilled oil into sediments in which weathering of oil is retarded, and from which nearly-fresh oil may be released to the water column over extended periods. In recent years, it is the long-term effects of acute and chronic pollution that have received increasing attention (Boesch et al., 1987).

What separates short-term from long-term effects is open to debate. Boesch et al. (1987) suggested that effects of duration longer than two years should be considered as long-term. These can be either effects that persist after an initial insult, or effects that result from persistent pollution. We do not know the upper bound for the potential length of a long-term effect. It is likely to be at least the length of a generation of the affected organisms, and it may be longer. An effect can be either direct damage to a resource or damage to the ability of an environment to support a resource. An effect can be said to be over when complete recovery has taken place. The quantification of both effects and recovery are difficult, particularly when they must be measured against a changing marine environment (Figures 5-1A and B) (Wiens,

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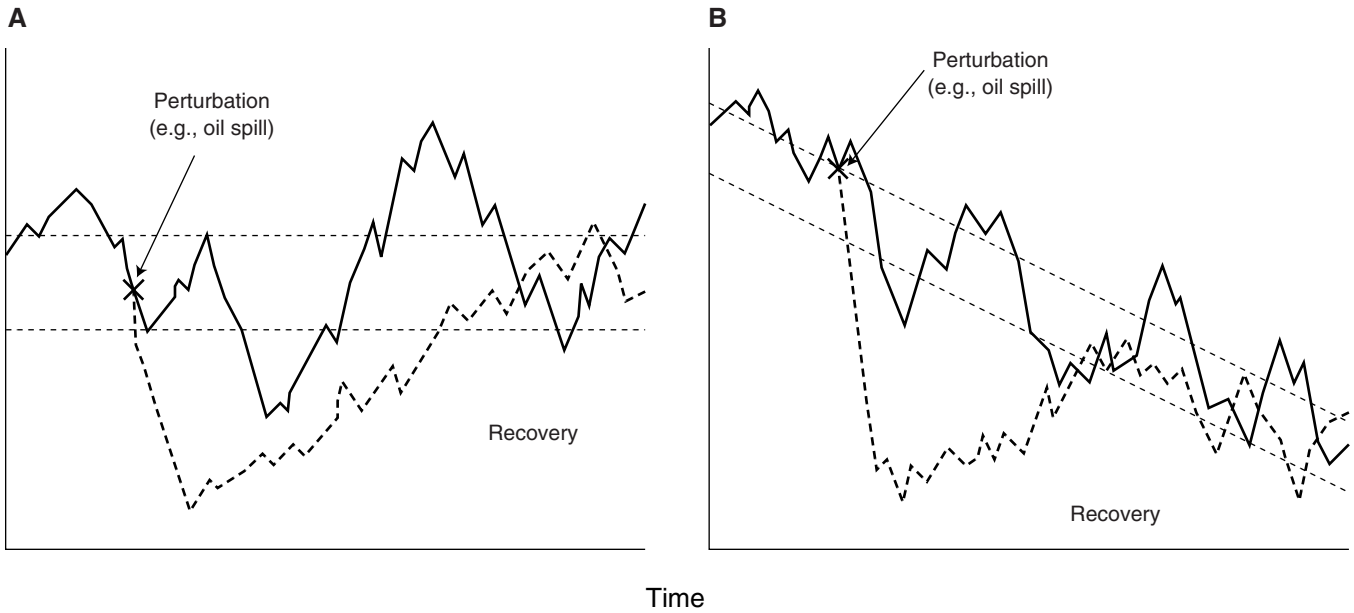

FIGURE 5-1 Hypothetical examples show how the impact of an oil spill and subsequent recovery can be assessed when the system under study undergoes natural variations (solid line). In (A), the system varies in time, but the long-term mean remains unchanged. In (B), there is a long-term decline in the state of the system (e.g., population size). Dashed lines indicate a "window" of normal variation about the mean (e.g., a 95 percent confidence interval). Operationally, "impact" occurs when the system is displaced outside this "window" (from Wiens, 1995, American Society for Testing and Materials).

1995; Spies et al., 1996; Peterson, 2001). Perhaps more difficult than detecting an effect is determining its significance (Boesch et al., 1987) (Figure 5-2). The spatial extent, persistence and recovery potential are all important, as is the perceived or monetary value of the affected resources. All else being equal, damage to a large area is more significant than damage to a small area of similar habitat. Damage to a small area that contains a highly valued resource can be of greater significance than damage to a much larger area devoid of valued resources. These issues are hotly contested after major pollution incidents.

DETERMINING EFFECTS IN A VARIABLE ENVIRONMENT

Oil can kill marine organisms, reduce their fitness through sublethal effects, and disrupt the structure and function of marine communities and ecosystems. While such effects have been unambiguously established in laboratory studies (Capuzzo, 1987; Moore et al., 1989) and after well-studied spills (Sanders et al., 1980; Burns et al., 1993; Peterson, 2001), determining the subtler long-term effects on populations, communities and ecosystems at low doses and in the presence of other contaminants poses significant scientific challenges. Multiple temporal and spatial variables make deciphering the effects extremely difficult, especially when considering the time and space scales at which marine populations and ecosystems change.

Marine ecosystems change naturally on a variety of time scales, ranging from hours to millennia, and on space scales ranging from meters to that of ocean basins. There are many causes of ecological change aside from oil pollution, including human disturbance, physical habitat alteration, other pollution, fishing, alteration of predation patterns, weather, and climate. Time scales at which oil affects the ocean range from days to years or even decades for some spills; chronic pollution occurs over years to decades. Oil spills affect the oceans at spatial scales of tens of square meters to thousands of square kilometers; chronic oil pollution can affect areas as small as a few square centimeters and as large as thousands of square kilometers.

Climatic changes can complicate the interpretation of contaminant impacts, especially if they have different effects on control and impact stations in an experimental design, or if a long time series of data is used to establish the "norm." Considerable scientific attention has been directed to understanding how climatic forcing affects marine ecosystems and fisheries (Beamish, 1993; Hare and Francis, 1995; McFarlane et al., 2000). Climate change can be cyclical, e.g., the Southern Ocean Oscillation the Pacific Decadal Oscillation (Barnston and Livesy, 1999), the North Atlantic Oscillation (Trenbreth and Hurrell, 1994; Hare and Mantua, 2000), or can be secular e.g., gradual rise in upper ocean temperature.

The biological effects of oil pollution are often referred to as acute or chronic. Spills are commonly thought of as hav-

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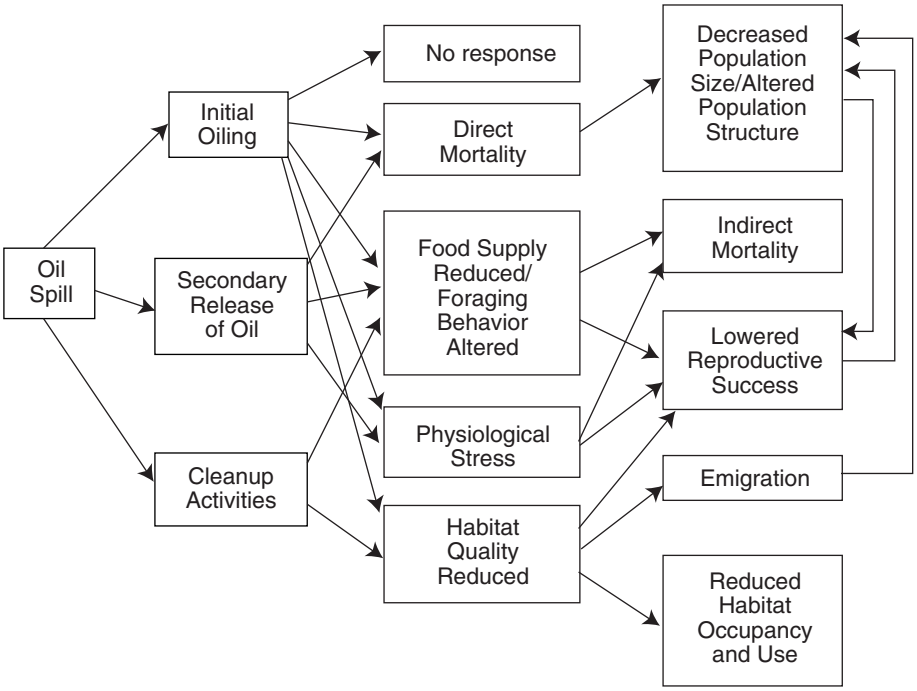

FIGURE 5-2 Schematic representation of oil spill influences on seabirds. The three primary avenues of effects, on population size and structure, reproduction and habitat occupancy, are highlighted (from Wiens, 1995, American Society for Testing and Materials).

ing short-term effects from high concentrations of petroleum. Chronic pollution, such as might occur from urban runoff into coastal embayments, may have continuous effects at low exposures. Not all oil pollution is clearly separable into these two categories. For example, exposure and effects are known to occur for long periods after some spills (Vandermeulen and Gordon, 1976; Sanders et al., 1980; Spies, 1987; Teal et al., 1992; Burns et al., 1993), and chronic exposures can be quite high, as is the case near petroleum seeps (Spies et al., 1980; Steurmer et al., 1982). The reader should bear this in mind during the ensuing discussion of the effects of acute and chronic exposure to oil. Additionally, this report generally focuses on the effects to benthic and wildlife populations, which were found to be most at risk from oil (Boesch et al., 1987).

It is within this complex multi-scale, spatial, and temporal environment that we are challenged to detect change caused by oil in the sea, and to assess the damage at the level of individuals, populations, communities, and ecosystems. Difficulty of detection increases with level of biological organization, with spatial and temporal scales of the affected system, and with the inherent variability of the system. Similarly, determination of complete recovery is complicated by this inherent variability.

The complex mosaic of change in the ocean has two aspects with regard to detecting the effects of oil pollution. First, it poses strategic challenges to determining the impact of oil through gathering observational data, as inevitably we make assumptions about the variability in the ecosystem and that variability can obscure large and continuing impacts. Second, the actual impact of the oil may be more complex than we realize if it interacts with spatially or temporally constrained phenomena.

In the closing decades of the twentieth century it was commonly held that the "balance of nature" has been severely altered by human actions. Consequently, much of our public policy was directed toward maintaining the status quo or returning ecosystems to a more pristine condition. While there is little doubt that human activities have had considerable impact in oceanic ecosystems, there has not been an equally widespread appreciation of how ecosystems change without human interference. The occurrence of several well-developed El Niños in the 1980s and 1990s made strong impacts on the public consciousness about longer-term cycles in the oceans. In Alaska, which has a strong resource-based economy, the rise and fall of salmon stocks in concert with the Pacific Decadal Oscillation (Beamish, 1993; Francis et al., 1998; Beamish et al., 1999) is now well known in the general population. Because public appreciation of ecosystem change seems to be following the growing scientific attention to long-term change in the oceans, the expectation that recovery of a polluted site will result in the return of an ecosystem to the state that it was in at the time of a pollution event is changing.

The observational framework for quantifying impacts involves determining differences based on sets of observations

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PHOTO 19 Oil from the Lake Barre spill, May 1997, spill formed a narrow band on the marsh stems, and there was little oiling of the soils. Also, the oil is highly degradable. Thus, most of the marsh vegetation survived. (Photo courtesy of Jacqui Michel, Research Planning, Inc.)

at impacted and putatively non-impacted areas, or at one or a series of sites where before-and-after impact observations are available. Ideally, before-after and control-impact (BACI) observations can be made (Stewart-Oaten et al., 1992; Wiens and Parker, 1995; Peterson et al., 2001). The inherent assumption is that the variability of the ecosystem is sufficiently controlled (in the experimental sense) by these designs, which may or may not be correct. Controlling for impact by comparison of sites that have been affected and not affected allows for a variety of potentially important non-oiling variables to influence the system—such as differences in water temperature, salinity, or substrate type. For example, see Bowman (1978) for a case where high temperatures were documented to have a differential effect on intertidal invertebrate mortality, that might have otherwise been attributed to oil or dispersant toxicity. Usually an attempt is made to find study sites that are as similar as possible in factors suspected to be important. When effects are determined based on comparisons of before-impact conditions and after-impact conditions, it is possible that the ecosystem has changed in ways unknown to the observer. The chances of making errors can be lessened when: (1) multiple sites are used in each of the impacted and non-impacted sites, (2) multiple times are used in the time series, or, even better, (3) when both multiple sites and multiple times are available. Nevertheless, unreported factors not related to oil can interfere with ecosystem processes in ways that disguise the effects of pollution. Of course, with each additional kind of impact that is measured, the chance of making an error (Type I) rises.

At the same time, the mosaic of complex interactions and the resultant changes in ecosystems makes it possible to miss an impact that occurs (Type II error). For example, if an oil spill occurs when the pelagic larval stages of a fish species are developing near the sea surface, many or most of these larvae may die. If these larvae were to be the foundation of what would otherwise have been a strong year class for that fish species and whose population is maintained by infrequent large year classes, then the impact could be much larger than otherwise supposed. That would be a disproportional effect on a process that is temporally constrained. There are also examples of potential impacts on processes that are disproportionate because they are spatially constrained. For instance, a small spill around a seabird habitat where a large proportion of a population is gathered for breeding could have a disproportionately large impact. A good example of this occurred when an estimated 30,000 oiled seabirds washed up along the coasts of the Skagerrak following a small release of oil from one or two ships (Mead and Baillie, 1981). At the other extreme, the wreck of the *Amoco Cadiz* off the coast of Brittany, France, resulted in the release of 230,000 tonnes of crude oil into coastal waters and the death of less than 5,000 birds (Hope-Jones et al., 1978). These examples help illustrate that the volume of oil is only one factor determining mortality of birds and the

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weak empirical relationship between spill volume and bird mortality points out the need to better understand the other sources of uncertainty (such as spill timing).

Assessing recovery after a pollution event is perhaps even more challenging than assessing initial damage. Recovery is further removed in time from the acute phase of the damage, and thus may be occurring in a different environmental framework than that which existed at the time of the accident. If there is variation in time, but the long-term mean remains stable, recovery might be judged by some to have been complete when the environmental variable of concern returns to within the normal range of variation (see Fig 5-1A, Wiens, 1995). In contrast, if the long-term environmental mean is changing, then recovery would occur when the variable of concern returns to within a range of variation around a short-term mean that will be quite different from that when the perturbation occurred (Fig. 5-1B). To assess recovery quantitatively requires either a well designed BACI approach, or one that compares measurements of the environmental variable of interest along a gradient of perturbation (Wiens, 1995). This gradient can be in space or time. One must be certain that, when numbers of organisms are being compared for assessment of recovery, attributes such as age or reproductive potential be taken into account. For example in marine birds, young, inexperienced animals do not have the same value to the population as experienced breeding adults. The natural variability inherent in estimates of populations introduces considerable uncertainty in assessing impact and recovery from pollution events. Confidence limits in excess of 20 percent of the mean size are usual in wildlife censuses. Such variability in the estimated mean makes it certain that population changes will be difficult to detect without a high degree of replication spatially and temporally before and after an event. More importantly, under some circumstances estimates of recovery based on the population returning to a "window" of natural fluctuation could minimize the time to true recovery. Other important considerations in evaluating oil pollution effects are the roles that laboratory studies, mesocosms and impact modeling play in complementing, or, in some cases, replacing the field observations discussed above.

Laboratory studies avoid the aforementioned problem of lack of control, but their improved precision disallows the wide range of possible interactions and indirect effects that can occur in complex ecosystems. Such indirect effects might be substantial. For example, in the *Exxon Valdez* and *Torrey Canyon* oil spills, destruction of the algal cover had indirect impacts on limpets and other invertebrates (Southward and Southward, 1978; Peterson, 2001). Such successional, reverberating or cascading indirect effects in a complex ecosystem may be very important, but are not captured by laboratory studies. The bulk of laboratory studies have examined oil impacts on organism mortality and health using dissolved oil or seawater suspensions. Most experiments are conducted for short durations (Capuzzo, 1987), which does not take into account long-term effects.

Field observations and laboratory experiments, as ways of knowing effects, represent two ends of a spectrum. Field observations allow little or no control of interactions between the full complement of ecosystem variables; laboratory experiments allow control of the interaction of single components that have been removed from the ecosystem. Taken together they still may not tell the whole story of oil impact. As a result, efforts have been made to bridge the gap between these two ends of the experimental control-field complexity continuum. Intermediate approaches include: laboratory experiments with multiple species, or communities that include environmental components (micro-and mesocosms); and field experiments, for example that put oiled sediments into the environment to be colonized by natural populations of animals and plants.

The modeling of the impacts of oil spills and their potential effects provides another route for predicting the potential effects of spilled oil. Oil spill impact modeling, which was originally applied to predicting the fate of oil in the environment, has recently been extended to prediction of effects (McCay, 2001).

In this chapter, we provide a brief review of progress in addressing the research recommendations of the 1985 *Oil in the Sea* report (NRC, 1985). We then examine the acute and chronic effects of oil at the organism, population and community/ecosystem levels. In the review, we single out marine birds and mammals for special attention because of their high visibility in spills and the great public concern for their welfare. It has been our intent to focus on the significant advances in knowledge and perceptions of the effects of oil in the sea, rather than to provide a detailed examination of the many research papers that have been published since the completion of the NRC (1985) or the Boesch and Rabalais (1987) reviews.

Progress Since 1985 Report

Since the major review of oil in the sea conducted by the National Research Council and published in 1985, there have been thousands of individual studies contributing to our overall understanding of the acute and chronic toxicity of oil in the marine environment and the restoration and recovery of oiled habitats. The major recommendations of the 1985 report were:

- To expand studies of effects of low concentrations of petroleum hydrocarbons on marine organisms, especially larval and juvenile stages;
- To examine the apparent coincidence of petroleum hydrocarbon exposure with increased prevalence of pollution-related disease in marine organisms;
- To examine the impacts of petroleum hydrocarbons in polar and tropical habitats;
- To better integrate laboratory studies with field investigations;

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A

B

PHOTO 20 (A) *Julie N* spill of IFO 380 coated the intertidal marshes of the Fore River near Portland, Maine. Photo taken in September 1996. (B) Photo Same area, one year post spill, September 1997. Most of the vegetation had completely recovered. Factors leading to recovery were: the plants were already in senescence when oiled, little or no sediment contamination occurred; large tidal range with good flushing. (Photos courtesy of Jacqui Michel, Research Planning, Inc.)

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- To assess the potential effects of petroleum hydrocarbons at population and ecosystem levels, especially for fish stocks and critical habitats such as mangroves and coral reefs.

Many of the studies conducted since 1985 have addressed these recommendations and have led us to a better understanding of the vulnerability of different habitats and different life history stages of a variety of marine organisms. Field and laboratory investigations have integrated studies of chemical fate and biological effects so that an improved understanding of the recovery process has been defined. In addition, oil spills have been monitored for longer periods of time and across wider far-field conditions to examine the chronic, long-term effects of spills. In their synthesis volume, Long-Term Environmental Effects of Offshore Oil and Gas Development, Boesch and Rabalais (1987) identified several important areas of research needs that complemented those identified in the *Oil in the Sea* report. Based on detailed consideration of the probability and severity of effects and the potential for resolution of uncertainties, they identified ten categories of potential long-term environmental effects. These were:

High Priority

- Chronic biological effects resulting from the persistence of medium and high molecular weight aromatic hydrocarbons and heterocyclic compounds and their degradation products in sediments and cold environments.
- Residual damage from oil spills to biogenically structured communities, such as coastal wetlands, reefs and vegetation beds.
- Effects of channelization for pipeline routing and navigation in coastal wetlands.

Intermediate Priority

- Effects of physical fouling by oil of aggregations of birds, mammals, and turtles.
- Effects on benthos of drilling discharges accumulated through field development rather than from exploratory drilling.
- Effects of produced water discharges into nearshore rather than open shelf environments.

Lower Priority

- Effects of noise and other physical disturbances on populations of birds, mammals, and turtles.
- Reduction of fishery stocks due to mortality of eggs and larvae as a result of oil spills.
- Effects of artificial islands and causeways in the Arctic on benthos and anadromous fish species.

Many of these concerns have now been fully addressed and are detailed in several synthesis reports written since 1987 (Box 5-1). Those topics not covered in synthesis reports will be addressed in this report.

Toxic Effects of Petroleum Hydrocarbons

The responses of organisms to petroleum hydrocarbons can be manifested at four levels of biological organization: (1) biochemical and cellular; (2) organismal, including the integration of physiological, biochemical and behavioral responses; (3) population, including alterations in population dynamics; and (4) community, resulting in alterations in community structure and dynamics. Impairment of behavioral, developmental, and physiological processes may occur at concentrations significantly lower than acutely toxic levels; such responses may alter the long-term survival of affected populations. Thus, the integration of physiological and behavioral disturbances may result in alterations at the population and community levels.

The effects of petroleum hydrocarbons in the marine environment can be either acute or chronic. Acute toxicity is defined as the immediate short-term effect of a single exposure to a toxicant. Chronic toxicity is defined as either the effects of long-term and continuous exposure to a toxicant or the long-term sublethal effects of acute exposure (Connell and Miller, 1984). Acute and chronic toxicity of petroleum hydrocarbons to marine organisms is dependent upon:

- concentration of petroleum hydrocarbons and length of exposure,
- persistence and bioavailability of specific hydrocarbons,
- the ability of organisms to accumulate and metabolize various hydrocarbons,
- the fate of metabolized products,
- the interference of specific hydrocarbons (or metabolites) with normal metabolic processes that may alter an organism's chances for survival and reproduction in the environment (Capuzzo, 1987), and
- the specific narcotic effects of hydrocarbons on nerve transmission.

Many of the early studies of acute toxicity focused on the toxicity of individual compounds to marine organisms or the differential toxicity of crude and refined oils (Anderson, 1979). The findings from these types of studies can be summarized as follows: The acute toxicity of individual hydrocarbons is largely related to their water solubility. The acute toxicity of a specific oil type is the result of the additive toxicity of individual compounds, especially aromatic compounds. Narcotic effects of individual petroleum compounds are an important component of acute toxicity and are most closely related to low molecular weight volatile compounds (Donkin et al., 1990). Sublethal effects following acute or chronic exposure to petroleum hydrocarbons include disruption in energetic processes; interference with biosynthetic

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BOX 5-1

Recent National Research Council Synthesis Reports Addressing Oil in the Sea and Offshore Oil and Gas Development

The following list reflects the extensive attention the NRC and government agencies have placed on the effect of petroleum in the environment.

- Assessment of the U.S. Outer Continental Shelf Environmental Studies Program: I. Physical Oceanography, 1990.
- Assessment of the U.S. Outer Continental Shelf Environmental Studies Program: II. Ecology, 1992
- Assessment of the U.S. Outer Continental Shelf Environmental Studies Program: III. Social and Economic Studies, 1992.
- Assessment of the U.S. Outer Continental Shelf Environmental Studies Program: IV. Lessons and Opportunities, 1993.
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processes and structural development; and direct toxic effects on developmental and reproductive stages (Capuzzo et al., 1988).

Weathering processes are extremely important in altering the toxicity of an oil spill. Neff et al. (2000) demonstrated rapid loss of monocyclic aromatic hydrocarbons (e.g., benzene, toluene, ethylbenzene, and xylene) from evaporation and a reduction of acute toxicity of the water-accommodated fraction (WAF) with loss of these compounds (see Box 5-2). With weathering processes and loss of the monoaromatic compounds, the polycyclic aromatic hydrocarbons become more important contributors to the toxicity of weathered oils. Other factors that may contribute to alterations in toxicity include photodegradation and photoactivation (Garrett et al., 1998; Boese et al., 1999; Mallakin et al., 1999; Little et al., 2000).

Barron et al. (1999) examined the chemistry and toxicity of water-accommodated fractions, from three environmentally-weathered middle distillate oils differing in aromatic content to test the hypothesis that the aromatic components of oil are the most toxic fraction. Using short-term growth and survival tests with the mysid, *Mysidopsis bahia*, they demonstrated that the oil with the lowest aromatic content (expressed as PAH concentration or naphthalene concentration in WAF) had the greatest toxicity. The toxicity of the three weathered oils was consistent with the reported toxicity of unweathered middle distillates tested under similar conditions (Anderson et al., 1974; Markarian et al., 1995) and were more similar to one another when reported as total petroleum hydrocarbons. Therefore, heterocyclic compounds and other soluble components in the water-accommodated fraction of weathered oil may contribute to acute toxicity.

The importance of PAH to weathered oil toxicity depends on the concentrations present, presence of other toxic components, and the degree to which the weathered oil has been degraded by microbial and photooxidation. Neff et al. (2000) provided an estimate of the contribution of different hydrocarbon classes to the toxicity of several Australian oils that had been weathered by evaporation in the laboratory (no microbial or photodegradation). Shelton et al. (1999) showed the importance of microbial degradation on weathered crude oil toxicity. Barron and Ka'aihue (2001) argued that photoenhanced toxicity could contribute to the toxicity of crude oil in the field.

Although a large volume of literature existed in 1985 on the effects of petroleum hydrocarbons on marine organisms in laboratory studies, the majority of studies conducted prior to 1985 were carried out at concentrations higher than is environmentally realistic. Those studies contributed to our understanding of the range of effects that could occur following an oil spill and the potential for long-term consequences, but they could not be used to develop realistic scenarios of the linkages between recovery of organisms and habitats and the degradation/disappearance of hydrocarbons from the habitat. Much progress has been made since the 1985 report addressing these issues. Some of the best examples of acute and chronic toxic effects of oil to marine organisms have been derived from observations in the field following oil spills and in laboratory studies designed to replicate the exposure field of actual spill conditions.

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BOX 5-2

Benzene, Toluene, Ethyl Benzene, and Xylenes (BTEX)

BTEX is the collective name for benzene, toluene, ethyl benzene, and xylenes, the volatile aromatic compounds often found in discharges, and petroleum oils and products (Wang and Fingas, 1996). The behavior of the four compounds is somewhat similar when released to the environment and thus they are usually considered as a group. Most light crude oils contain BTEX usually from about 0.5 up to 5% or more. Gasoline can contain up to 40% BTEX. BTEX compounds are volatile and, if discharged into the sea, will rapidly volatilize into the air, and there is, in fact, a net loss of BTEX compounds. Because of this behavior, the discharges of BTEX were not considered in this study.

BTEX compounds are acutely toxic to aquatic organisms if contact is maintained. BTEX compounds are relatively soluble in water, the solubility of benzene is about 1400 mg/L and xylenes about 120 mg/L. Because of the volatility of BTEX, the time exposure to aquatic organisms may be short enough to avoid toxic effects. BTEX are generally neurotoxic to target organisms. Benzene, in particular, has also been found to be carcinogenic to mammals and humans.

Gasoline contains large amounts of BTEX. The bulk solubility of gasoline has been found to vary from 100 to 500 ppm, depending on the specific type of gasoline and its constituents. The aquatic toxicity of gasoline is relatively high. The fifty-percent lethal concentration to test organisms over a 48-hour period has been found to be 10 to 50 mg/L for *Daphnia magna*, the water flea, 5 to 15 mg/L for *Artemia*, small brine shrimp, and 5 to 10 mg/L for rainbow trout larvae.

Produced waters contain a variety of volatile hydrocarbons, including the BTEX series (Rabalais et al., 1991a,b). Produced waters generally have concentrations of dissolved salts much higher than sea water and therefore sink through the water column into which they are disposed. BTEX compounds in produced water discharged to well-mixed open ocean waters are diluted rapidly. Twenty meters down-current from a production platform discharging 11 million L/d of produced water containing an average of 6,410 μg/L total BTEX to the Bass Strait off southeast Australia, the average concentration of BTEX was 0.43 μg/L, a dilution of 14,900-fold (Terrens and Tait, 1996). In well-flushed, dispersive and deeper water environments of the Louisiana coast, the BTEX chemical contaminant signal may be negligible as close as 50-100 m from the point of discharge (Rabalais et al. 1991a,b). In shallower, less dispersive environments the produced water plume along with the BTEX spreads in a thin dense plume across the surface sediments of the receiving environment, and the chemical signature of the produced waters can be detected up to 1000 m from the point of discharge (Rabalais et al., 1991a, b). BTEX were detected in the water overlying the sediment surface near estuarine and coastal environments that were categorized as less dispersive or where the concentration of the BTEX was high in the discharge. Produced waters vary considerably in BTEX concentrations, but produced waters discharged into surface waters of Louisiana ranged from 26—4,700 μg/L benzene, 11—1,300 μg/L toluene, 2.1—75 μg/L ethylbenzene, and 8.8—520 μg/L xylenes. BTEX persisted in the density plume that dispersed across the sediment surface in poorly flushed Louisiana study areas in concentrations up to 86 μg/L benzene, 32 μg/L toluene, 2.3 μg/L ethylbenzene, and 17 μg/L xylenes; in more dispersive environments, they were not detected. BTEX in the overlying water column, if present, along with the more persistent polynuclear aromatic hydrocarbons in the sediments, likely contributed to the mortality of the benthic infauna where diminished benthic communities were documented adjacent to produced water discharges. The mortality could not be attributed to high salinity, because the salinity of the interstitial waters of the sediments examined were within the tolerance range of the euryhaline benthos found in the study area.

Data gathered from several spills that occurred in the 1970s and 1980s demonstrated that the medium and higher molecular weight aromatic compounds, such as the alkylated phenanthrenes and alkylated dibenzothiophenes, are among the most persistent compounds in both animal tissues and sediments (Capuzzo, 1987). The half-lives of these compounds in marine bivalves following spill conditions can be quite long compared to the relatively rapid decline in monoaromatic compounds and unsubstituted phenanthrenes and naphthalenes (Oudot et al., 1981; Farrington et al., 1982; Anderson et al., 1983; Burns and Yelle-Simmons, 1994). The degree to which the persistence of these compounds in tissues interferes with normal metabolic processes that affect growth, development and reproduction has been the focus of much debate and research. Sublethal effects from hydrocarbon exposure can occur at concentrations several orders of magnitude lower than concentrations that induce acute toxic effects (Vandermeulen and Capuzzo, 1983). Impairment of feeding mechanisms, growth rates, development rates, energetics, reproductive output, recruitment rates and increased susceptibility to disease and other histopathological disorders are some examples of the types of sublethal effects that may occur with exposure to petroleum hydrocarbons (Capuzzo, 1987). Early developmental stages can be especially vulnerable to hydrocarbon exposure, and recruitment failure in chronically contaminated habitats may be related to direct toxic effects of hydrocarbon contaminated sediments (Krebs and Burns, 1977; Cabioch et al., 1980, Sanders et al., 1980; Elmgren et al., 1983).

Several studies have demonstrated the potential for oil residuals on beach sediments to have significant toxic effects on fish eggs and embryos. Heintz et al. (1999) reported embryo mortality of pink salmon with laboratory exposure to aqueous total PAH concentrations as low as 1 ppb total PAH derived from artificially weathered Alaska North Slope crude oil. This is consistent with the field observations of Bue et al. (1996) of embryo mortality of pink salmon in streams traversing oiled beaches following the spill from the

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Exxon Valdez. Carls et al. (1999) exposed Pacific herring eggs for 16 days to weathered Alaska North Slope crude oil and observed that exposure to initial aqueous concentrations as low as 0.7 ppb PAH caused developmental malformations, genetic damage, mortality, decreased size at hatching, and impaired swimming. Concentrations as low as 0.4 ppb caused premature hatching and yolk-sac edema. Exposure to less weathered oil produced similar results but at higher exposure concentrations (9.1 ppb).

Other investigators have observed developmental effects on fish and invertebrates exposed to low concentrations of petroleum hydrocarbons (Capuzzo et al., 1988). The high toxicity of weathered oil reported by Heintz et al. (1999) and Carls et al. (1999), however, suggests that higher concentrations of one or more constituents in weathered fractions relative to total PAH contribute to the increased toxicity.

Bioavailability, Bioaccumulation, and Metabolism

The concept of bioavailability is extremely important in understanding and describing the environmental fates and biological effects of petroleum in the marine environment. A concise definition of what is meant in this context by bioavailability is essential. In aquatic toxicology, bioavailability usually is defined as the extent to which a chemical can be absorbed or adsorbed by a living organism by active (biological) or passive (physical or chemical) processes. A chemical is said to be bioavailable if it is in a form that can move through or bind to the surface coating (e.g., skin, gill epithelium, gut lining, cell membrane) of an aquatic organism (Kleinow et al., 1999).

Accumulation of petroleum hydrocarbons by marine organisms is dependent on the biological availability of hydrocarbons, the length of exposure, and the organism's capacity for metabolic transformations. There are two aspects of petroleum hydrocarbon bioavailability that are important in understanding the behavior of oil in the environment: environmental availability, and biological availability. Environmental availability is the physical and chemical form of the chemical in the environment and its accessibility to biological receptors. Generally, chemicals in true solution in the ambient water are considered more bioavailable than chemicals in solid or adsorbed forms. Petroleum hydrocarbons of the types found in the marine environment may be present in true solution, complexed with dissolved organic matter and colloids, as dispersed micelles, adsorbed on the surface of inorganic or organic particles, occluded within particles (e.g., in soot, coal, or tar), associated with oil droplets, and in the tissues of marine organisms (Readman et al., 1984; Gschwend and Schwarzenbach, 1992). The hydrocarbons in the different phases are exchangeable but, at any given moment, only a fraction of the total hydrocarbons in water, sediments, and biota is in bioavailable forms.

The dissolved hydrocarbons are the most bioavailable, followed by those in tissues of marine organisms (if the organisms are eaten) or associated with liquid, unweathered oil droplets. Thus, bioavailability of PAH from sediments and food is less than that from solution in the water (Pruell et al., 1987). Particulate PAH associated with soot or weathered oil particles (e.g., tarballs) have a low bioavailability (Farrington, 1986; Gustafsson et al., 1997a,b; Baumard et al., 1999). As oil weathers, its viscosity and average molecular weight increase, decreasing the rate of partitioning of higher molecular weight PAH from the oil phase into water in contact with the oil, decreasing the accessibility of these PAH to aquatic organisms (McGrath et al., 2001). Soot-associated PAH are not bioaccumulated in the tissues of aquatic animals. Maruya et al. (1996) showed that sediment-associated animals in San Francisco Bay, CA, were not able to bioaccumulate PAH from the very fine-grained particles (identified as soot) in the sediments. Pruell et al. (1986) showed that the bioaccumulation of PAH from contaminated sediments by mussels correlated with the concentration of dissolved but not particulate PAH in the sediments.

The other aspect of environmental availability is accessibility. Petroleum hydrocarbons that are buried deep in sediments or sequestered in solid, highly weathered oil deposits on the shore are not accessible to marine and terrestrial organisms and, therefore have a low bioavailability. Biological availability depends on the rate at which a chemical is assimilated into the tissues of the organism and accumulates at the sites of toxic action in the organism. This depends on the physical/chemical properties of the chemical in contact with the organism, the relative surface area of permeable epithelia in the organism, and the ability of the organism to excrete or detoxify the chemical. Nonpolar (hydrophobic) organic chemicals such as petroleum hydrocarbons, have a low aqueous solubility and a high lipid solubility. Hydrocarbons in solution in water diffuse down an activity or fugacity gradient from the water phase into lipid-rich tissues of marine organisms in contact with the water. According to equilibrium partitioning theory (Davies and Dobbs, 1984; Bierman, 1990), when an aquatic animal is exposed to a nonpolar organic chemical dissolved in the ambient water, the chemical partitions across permeable membranes into tissue lipids until an equilibrium, approximated by the octanol/water partition coefficient (K_{ow}) for the chemical is reached. At equilibrium, the rates of absorption into and desorption from the lipid phase of the organism are equal. Toxic responses in the organism occur when the concentration of nonpolar organic chemicals in the tissues reach a critical concentration (McCarty and Mackay, 1993). The log K_{ow} of PAH increases with increasing molecular weight (Neff and Burns, 1996). However, bioavailability, measured as log bioconcentration factor (BCF: concentration in tissues/concentration in water at equilibrium), does not increase in a linear fashion with increasing PAH log K_{ow} (Baussant et al., 2001a,b). The sediment organic carbon-water coefficient, K_{oc} is also useful in predicting uptake of sediment-associated hydrocarbons (Fisher, 1995; Meador et al. 1995; DiToro

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et al., 2000;). The higher molecular weight PAH are less bioavailable than predicted by equilibrium partitioning theory because of limitations on their uptake rates by organisms, their lower solubility in tissue lipids, and rapid metabolism of higher molecular weight PAH in some marine animals. Bioaccumulation factors for pyrogenically derived hydrocarbons are much less than predicted based on K_{oc} and suggest that an additional estimate of the fraction of compound available for equilibrium partitioning may be needed (McGroddy and Farrington, 1995; McGroddy et al., 1996).

Biotransformation is an important factor in examining tissue burdens and biological effects. An organism's capacity for biotransformation of hydrocarbons has been used in many instances as an estimate of exposure in the absence of measurable hydrocarbon concentrations. Vertebrates have a high capacity for metabolizing aromatic hydrocarbons including PAH through cytochrome P450 1A mediated oxidation (Stegeman, 1989; Stegeman and Lech, 1991; Spies et al., 1996). Elevation of cytochrome P450 1A levels in fish may indicate exposure to some aromatic hydrocarbons, even though tissue levels do not show elevated concentrations. There is a large literature that links elevated P450 1A levels in fish tissues to aromatic contaminants in marine sediments (e.g., Stegeman and Lech, 1991), but it is theoretically possible for some other natural compounds to induce these enzymes as well. Measurement of hydrocarbon metabolites in tissues where elevated cytochrome P450 1A is observed provides further evidence of the relationship of hydrocarbon exposure, metabolism and cytochrome P450 1A activity (Stein et al., 1992; Collier et al., 1993; Wirgin et al., 1994). Metabolism of hydrocarbon mixtures may result in excretion of some compounds but also activation of some compounds to toxic metabolites including DNA adducts (Wirgin et al., 1994).

Long-Term Effects on Benthic Populations

Chronic toxicity of petroleum hydrocarbons after an oil spill is associated with the persistent fractions of oil and individual responses of different species to specific compounds. Alterations in bioenergetics and growth of bivalve molluscs following exposure to petroleum hydrocarbons appear to be related to tissue burdens of specific aromatic compounds (Gilfillan et al., 1977; Widdows et al., 1982, 1987; Donkin et al., 1990). Widdows et al. (1982) demonstrated a negative correlation between cellular and physiological stress indices (lysosomal properties and scope for growth) and tissue concentrations of aromatic hydrocarbons with long-term exposure of *Mytilus edulis* to low concentrations of North Sea crude oil. Recovery of mussels following long-

PHOTO 21 Oil penetrated deeply into burrows in the muddy sediments on tidal flats and marshes along the Persian Gulf. Note the liquid oil draining out of a burrow in 1993, two years after the spills. (Photo courtesy of Jacqui Michel, Research Planning, Inc.)

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term exposure to low concentrations of diesel oil coincided with depuration of aromatic hydrocarbons (Widdows et al., 1987). Donkin et al. (1990) suggested that reductions in scope for growth in *M. edulis* were related to the accumulation of two- and three-ring aromatic hydrocarbons, as these compounds induced a narcotizing effect on ciliary feeding mechanisms.

Krebs and Burns (1977) observed long-term reductions in recruitment and over-wintering mortality in the fiddler crab *Uca pugnax* for seven years following the spill of No. 2 fuel oil from the barge *Florida*. Recovery of crab populations was correlated with the disappearance of naphthalenes and alkylated naphthalenes from contaminated sediments. Similar patterns of long-term changes in recruitment and density of benthic fauna have been observed at sites of other oil spills and in experimental mesocosms (Cabioch et al., 1980; Grassle et al., 1981; Oviatt et al., 1982; Elmgren et al., 1983). Ho et al. (1999) compared the toxicity to the amphipod *Ampelisca abdita* and chemistry of spilled No. 2 fuel oil in subtidal sediment samples for nine months following the spill from the barge *North Cape* (Box 4-1). Toxicity to the amphipods decreased as the PAH concentration in sediments decreased over the first six months post-spill (Figure 5-3).

The persistence of PAH in sediments, especially in urban areas with multiple sources of hydrocarbon inputs, is an example of chronic persistence and toxicity beyond the observations made following oil spills (Box 5-3). Meador et al. (1995) reviewed the processes controlling the uptake and persistence of PAH in marine organisms, especially under chronic exposure conditions, highlighting differential mechanisms of uptake, tissue distribution, and elimination. Transfer of contaminants to marine biota and the human consumer and toxicological effects on the ecosystem are dependent on the availability and persistence of these contaminants within benthic environments. The bioaccumulation of lipophilic organic contaminants is influenced by chemical factors such as solubility and particle adsorption-desorption kinetics of specific compounds and biological factors such as the transfer of compounds through food chains, the amount of body lipid in exposed organisms, and metabolic transformations. The incidence of tumors and other histopathological disorders in bottom-dwelling fish and shellfish from contaminated coastal areas has suggested a possible link between levels of lipophilic organic contaminants (such as PAH) and the increased incidence of histopathological conditions (Neff and Haensly, 1982; Berthou et al., 1987; Varanasi et al., 1987; Gardner and Pruell, 1988; Moore et al, 1994; McDowell and Shea, 1997).

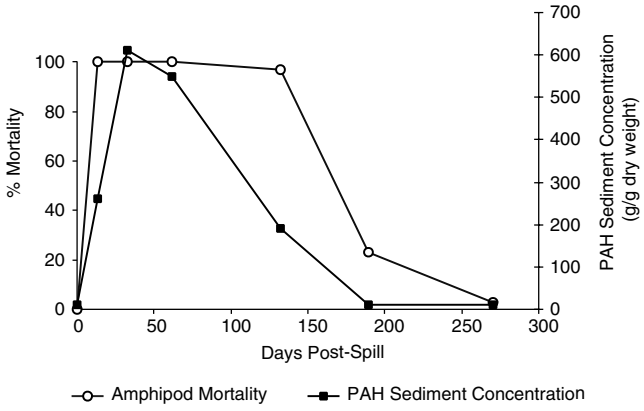

FIGURE 5-3 Amphipod mortality and PAH concentrations in sediments after the *North Cape* oil spill off Cape Cod, Massachusetts, January 19, 1996 (modified from Ho et al., 1999, *Marine Pollution Bulletin*).

In addition to possible histopathological damage, sublethal toxic effects of contaminants in marine organisms include impairment of physiological processes that may alter the energy available for growth and reproduction and other effects on reproductive and developmental processes including direct genetic damage (Capuzzo, 1987; Capuzzo et al., 1988). Chronic exposure to chemical contaminants can result in alterations in reproductive and developmental potential of populations of marine organisms, resulting in possible changes in population structure and dynamics. It is difficult to ascertain, however, the relationship between chronic responses of organisms to contaminants and large-scale alterations in the functioning of marine ecosystems or the sustainable yield of harvestable species. Cairns (1983) argued that our ability to detect toxic effects at higher levels of biological organization is limited by the lack of reliable predictive tests at population, community, and ecosystem levels. Much research effort is needed in these areas before environmental hazards as a result of contaminant inputs can be addressed adequately. Koojiman and Metz (1984) suggested that the sublethal effects of contaminant exposure should be interpreted in light of the survival probabilities and reproductive success of populations, thus bridging the gap between individual and population responses. Although a wide range of sublethal stress indices have been proposed for evaluation of chronic responses of organisms to contaminants, few have been linked to the survival potential of the individual organism or the reproductive potential of the population. Rice et al. (2001) reviewed studies on the long-term effects of the *Exxon Valdez* oil spill on pink salmon, specifically addressing differential effects of low concentrations of oil on specific life history stages. Their results illustrate the complexity of assessing population-level impacts from persistent hydrocarbon residues, even at very low concentrations.

Putative damage to pink salmon as a result of the *Exxon Valdez* oil spill has been controversial (e.g., Rice et al., 2001). Much of this controversy has focused on the potential damage to embryos incubating in the mouths of streams that were oiled. The potential damage to resident fish embryos in these oiled redds may be long lasting and serious. For example, contrasts between oiled and unoiled streams around

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BOX 5-3

Boston Harbor

Chronic contamination of urban harbors reflects a history of contaminant discharges from a variety of sources. Petroleum hydrocarbons, including polycyclic aromatic hydrocarbons, may be derived from the burning of fossil fuels, accidental oil spills, and chronic inputs from municipal discharges and marinas. Loadings of polycyclic aromatic hydrocarbons to Massachusetts Bay are estimated to be within the range of 2.1 to 13.7 metric tons per year (Menzie-Cura & Associates, 1991). Sites receiving inputs from combined sewer overflows (CSOs) are among the most contaminated sites in Boston Harbor and Massachusetts Bays. Concentrations of total PAH in Boston Harbor sediments are among the highest reported for all coastal sites of the U.S. in the NOAA National Status and Trends program. Among sites examined within the New England region, concentrations of total PAH in sediment samples from Boston Harbor exceeded concentrations in samples from other sites by as much as one to two orders of magnitude (MacDonald, 1991). In addition to sediments, biota from Boston Harbor are highly contaminated with a variety of lipophilic organic contaminants including both low molecular weight and high molecular weight PAH. Concentrations of total PAH in tissues of the blue mussel (*Mytilus edulis*) are in the upper 15 percent of the most contaminated sites from the U.S. coastline surveyed in the National Status and Trends Program (MacDonald, 1991).

The relative abundance of individual PAH in sediments surveyed in Boston Harbor are typical of sediments with highly weathered petroleum inputs mixed with combustion products (McDowell and Shea, 1997). Sediments from Boston Harbor stations are enriched with higher molecular weight PAH indicative of combustion sources and creosote, including fluoranthene, pyrene, and chrysene. McGroddy and Farrington (1995) examined the sediment-porewater partitioning of PAH in three cores from Boston Harbor and found that only a fraction of the total measured sediment PAH concentration was available for equilibrium partitioning and biological uptake. Laboratory desorption experiments demonstrated that only a small fraction of sediment phenanthrene and pyrene were available for equilibrium partitioning (McGroddy et al., 1996). Studies of bioaccumulation of PAH in bivalve mollusks such as the soft-shell clam *Mya arenaria* and the blue mussel *Mytilus edulis* also reflect the reduced availability of PAH from Boston Harbor sediments (McDowell et al., 1999). PAH were detected in clam tissues and sediments collected along a gradient of contamination in Boston Harbor and Massachusetts and Cape Cod Bays, but the bioavailability of specific compounds varied at different sites. Estimates of AEP (available for equilibrium partitioning) provided the best predictor of relative bioavailability of pyrogenic PAH.

With the presence of high concentrations of contaminants in Boston Harbor sediments and the need for navigational dredging innovative solutions to dredging Boston Harbor had to be developed. The Boston Harbor Navigation Improvement Project was the result of three decades of negotiation involving many stakeholders and considering 312 land-based inland and coastal sites, 21 landfills, and 21 aquatic sites as disposal options (NRC, 1997). Four final management options were identified as acceptable: the Massachusetts Bay Disposal site, the Boston Lightship site, two near-shore borrow pits, and one contained aquatic disposal site. The final selection involves removal of contaminated sediments to allow dredging of highly contaminated sediments, formation of very deep pits, replacement of the contaminated sediment and, finally, placement of clean sand as a sediment cover. Uncontaminated sediments that are removed to form the deep pits will be disposed at the Massachusetts Bay Disposal site. This solution is a good example of meeting both economic and environmental objectives in the management of contaminated sediments.

Knight Island, Alaska found significantly elevated mortalities of embryos in oiled streams in 1989-1993 (Bue et al., 1998). These findings are indicative of P450 1A induction as measured in oiled streams (Weidmer et al., 1996), as well as with a model of subsurface movement of oil in streams based on intertidal elevations (Rice et al., 2001). These findings were called into question by some subsequent studies on a variety of grounds including questions about study design. Brannon et al. (1995) concluded that oil levels in the redd had no effect on the incubation of fertilized eggs. In a later study, Brannon et al. (2001) claimed that sampling occurred on different time schedules for oiled streams and unoiled streams. Therefore, the authors contended that any damage to eggs was the result of collection and handling, and that oil levels did not negatively impact the embryos. While Rice et al. (2001) clearly showed that their sampling methods had greater power to detect embryo mortality in the field, they were not able to discount the egg-shock hypothesis. However hatchery-raised embryos from parents that were taken from both oiled and unoiled streams had patterns of survival that closely matched those from the field (Bue et al., 1998). Additionally, there was disagreement about damage at other life history stages and laboratory toxicological findings within this species (Brannon and Maki, 1996; Brannon et al., 2001; Rice et al., 2001).

Johnson et al. (2001) reported threshold-sediment PAH concentrations for toxicopathic liver lesions in English sole ranging from 54 to 2,800 ng/g dry weight and a threshold for DNA adducts in liver of 300 ng per g dry weight. These thresholds were based on analyses of fish collected in Puget Sound, Washington. Other effects included inhibited gonadal growth, inhibited spawning, reduced egg viability, and reduced growth, although there were insufficient data to determine a precise threshold. From these analyses, Johnson et al. (2001) proposed a sediment quality guideline of 1000 ppb total PAH (ng/g dry weight) to minimize effects on estuarine

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PHOTO 22 MODIS (or Moderate Resolution Imaging Spectroradiometer) satellite imagery (250 m resolution) of New England. Urbanization, visible from space, increases both population density and the percent of paved surface, altering the volume and composition of runoff. (Image courtesy of NASA.)

fish (Figure 5-4). This is consistent with observations made by other investigators for other estuarine species (*Mya arenaria*, soft shell clam; McDowell and Shea, 1997; *Ampelisca abdita*, amphipod; Ho et al., 1999). However, toxic effects observed will be dependent on not only the concentration of total PAH but the composition and relative distribution of individual compounds. This makes it very difficult to compare studies unless detailed composition data are also presented.

Birds and Marine Mammals

Marine birds and mammals can be affected by oil in the sea through several pathways (see references in Hunt, 1987; Kajigaya and Oka, 1999; Tsurumi et al., 1999). As air-breathing organisms that obtain much or all of their food from beneath the surface of the sea, marine birds and mammals must frequently pass through the water's surface. When floating oil is present, they become fouled. Additionally, many species of birds frequent the intertidal zone while foraging and resting, as do seals, sea lions, river otters, and occasionally sea otters. While there, these warm-blooded vertebrates may become coated with oil that has come ashore. The presence of oil on the feathers of a seabird or the pelage of a marine mammal can destroy the waterproofing

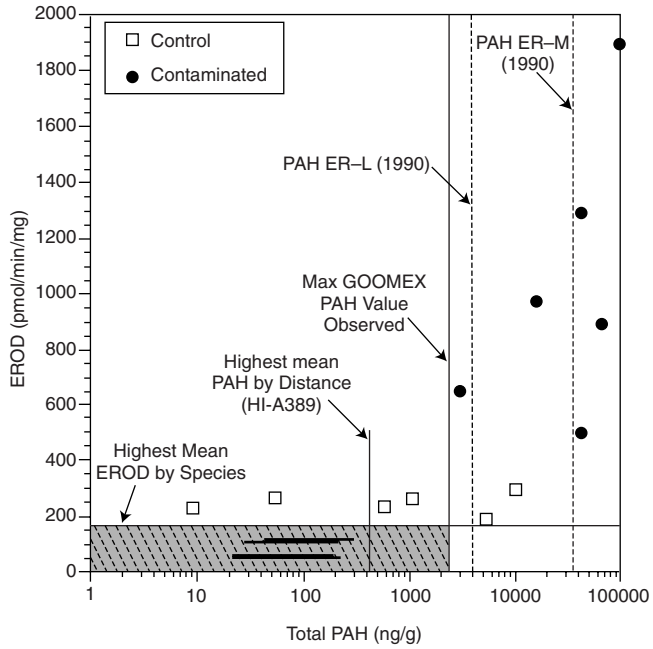

FIGURE 5-4 Correlation between total PAH concentrations in sediments and hepatic EROD activities of fish (from McDonald et al., 1996, Canadian Journal of Fisheries and Aquatic Sciences).

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and insulating characteristics of the feathers or fur and lead to death from hypothermia. Seabirds and marine mammals may be poisoned when they ingest oil during the course of trying to remove it from their feathers or pelage, or when it adheres to food items. Likewise, marine mammals (and possibly seabirds) may inhale toxic doses of petroleum vapor when at the surface in the vicinity of an oil spill (Geraci, 1990; Geraci and Williams, 1990; St. Aubin, 1990a), although there appear to be few data indicating that this is an important source of mortality (Figure 5-5). In some cases, these upper trophic level predators may become exposed to oil by ingesting prey that have oil or its metabolites in their tissues. Seabirds can transfer oil from their feathers to the surface of their eggs during incubation. Depending on the type of oil on the feathers and the presence of toxic components, embryos in the affected eggs may fail to develop. Oil can also indirectly affect the survival or reproductive success of marine birds and mammals by affecting the distribution, abundance or availability of prey.

In seabirds, ingestion of oil or oil-contaminated prey may lead to immuno-suppression and Heinz-body hemolytic anemia which compromises the ability of the blood to carry oxygen (Leighton et al., 1983; Fry and Addiego, 1987). This effect persists long after the birds appear to have recovered from exposure (Fry and Addiego, 1987). Diminished oxygen transport capacity in the blood is a particular problem for species of birds that obtain their food by pursuing prey underwater. Although the effects of the anemia have yet to be demonstrated in the field (Nisbet, 1994), seabird survival post-oiling, with or without cleaning, may be compromised. Marine mammals are also vulnerable to the toxic effects of ingested oil, and species of marine mammals such as sea otters that depend on a clean pellage for insulation are also vulnerable to surface oiling (Geraci and St. Aubin, 1987; Geraci, 1990; Geraci and Williams, 1990; St. Aubin, 1990a,b; St. Aubin and Lounsbury, 1990). Effects may be exacerbated by stress resulting from handling during cleaning (Briggs et al., 1996).

The number of seabirds killed and the damage to local populations in a spill is more likely to be determined by location and timing of the spill than by its size (Hunt, 1987; Burger, 1993). Burger found a statistically significant but

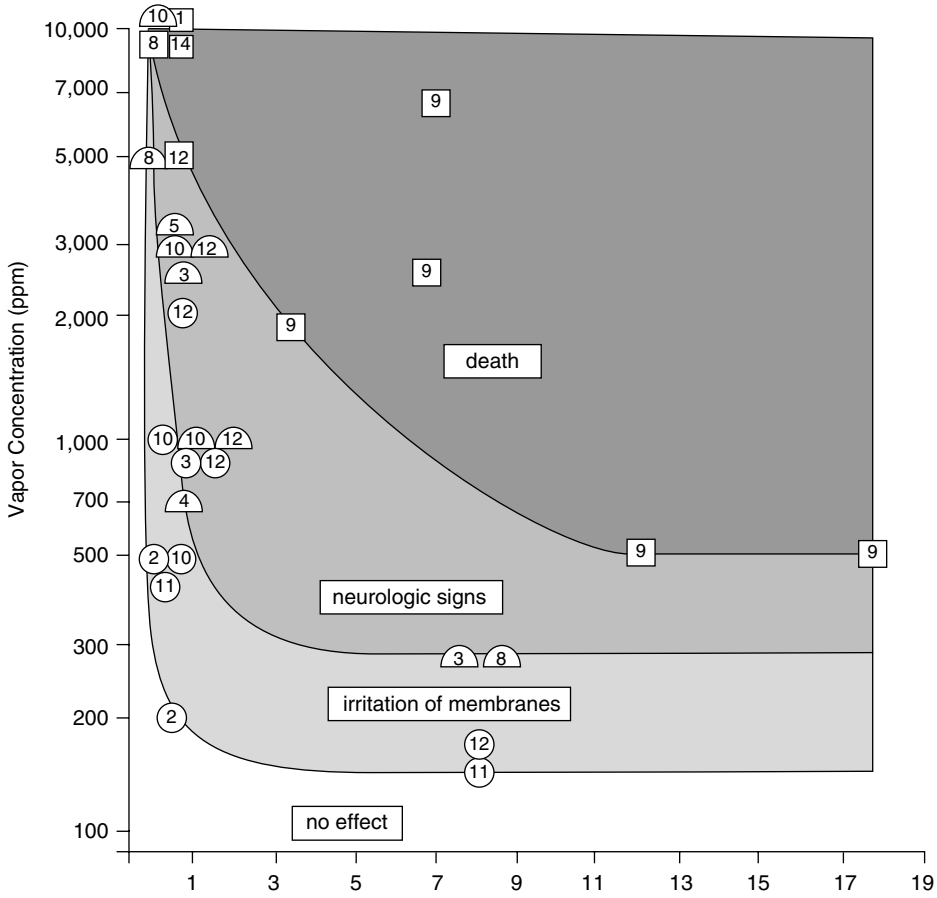

FIGURE 5-5 Summary of the effects on mammals of exposure to an inhalation of various petroleum vapors, principally those of gasoline (from Geraci and St. Aubin, 1987, Academic Press).

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weak log-log correlation between the number of birds killed and the volume of oil spilled when he analyzed 45 spills. In another analysis of 98 spills, there was no correlation (Dagmar Etkin, Environmental Research Consulting, personal communication). Large spills that occur over the deep ocean in open water that has little bird life will have a lesser effect on seabirds than a small spill in a critical habitat where high numbers of birds are aggregated on the water. The season in which a spill occurs is also critical (Hunt, 1987). If the spill occurs when birds are aggregated during breeding or migration, the impact will be much greater than if they are widely dispersed at sea. It is likely that the cumulative effect of numerous "small" spills and chronic pollution has had a greater effect on seabird populations than the rarer large spills. Recent evidence, however, suggests that the incidence of seabird mortality from small spills may be declining in the North Sea region (Camphuysen, 1998). This shift may reflect the reduction of small discharges of oil noted earlier in Chapter 3.

There has been a "general-rule-of-thumb" that the body count of birds recovered after a spill represents about 10 percent of the birds killed in a spill (Tanis and Morzer Bruijns, 1969; NRC, 1985). Burger (1993), however, found that there was no justification for this assumption; the mean estimate for 21 spills for which the number of birds found dead and that the overall mortality were determined to be between four and five times the number of birds actually counted. The relationship among the number of carcasses recovered and the total mortality will vary between species, being dependent among other factors on body size, average distance to shore carcass buoyancy, and the prevailing winds during and after the spill.

Few studies of oil spills have provided the information necessary to assess delayed or long-term effects on community-level processes in the affected communities or ecosystems. Where keystone predators are removed, competitive dominants at the next lower trophic level can increase and change the structure of the community. For example, in areas of Prince William Sound where sea otters were removed by oiling, their preferred prey, sea urchins, have increased in some locations (Peterson, 2001). Elsewhere in Alaska where sea urchin populations have been able to increase in the absence of sea otters, severe damage to kelp beds have resulted (Estes, 1995; Estes and Duggins, 1995).

In addition to the strong evidence for the impact of massive contamination associated with an oil spill, there is increasing evidence that chronic, low-level exposures to hydrocarbons in the sea can have a significant effect on the survival and reproductive performance of seabirds and some marine mammals. Sublethal effects of oil on seabirds include reduced reproductive success, and physiological impairment, including increased vulnerability to stress (reviewed in Fry and Addiego, 1987,1988; Hunt, 1987; Briggs et al., 1996). In contrast, in marine mammals, sublethal exposure to petroleum hydrocarbons has been shown to cause minimal damage to pinnipeds and cetaceans (e.g., Geraci, 1990; St. Aubin, 1990b), although sea otters appear to be more sensitive (Geraci and Williams, 1990; Monson et al., 2000). Because both marine birds and marine mammals have the enzymes necessary for the detoxification and elimination of petroleum hydrocarbons, parent compounds of petroleum hydrocarbons are not accumulated and sequestered in tissues as chlorinated hydrocarbons. Toxic metabolites produced by metabolism of polycyclic aromatic hydrocarbons, however, may accumulate and induce toxic effects (Brunstrom et al., 1991; Melancon, 1996, 1995). Chronic pathologies would not be expected once oil ceased to be ingested.

There is mixed evidence that oil pollution can have demonstrable effects on the population trajectories of marine birds and mammals. Spilled oil has had and still poses a potentially devastating effect on African Penguins (*Spheniscus demersus*) in southern Africa (Westphal and Rowan, 1970; Vermeer and Vermeer, 1975; Clark, 1984; Dagmar Etkin, Environmental Research Consulting, personal communication). At Les Sept Iles, France, declines in the numbers of Common Murres (*Urea aalge*) attending colonies have been attributed to the effects of oil spilled in the *Torrey Canyon* and *Amoco Cadiz* accidents (Nisbet, 1994). In northern Europe between 1915 and 1988, 60-90 percent of beached alcids were oiled (Camphuysen, 1989), and Hudson (1985) found that oiling accounted for between 18 and 28 percent of mortality of banded alcids. In addition, there is conflicting sentiment that populations of sea ducks in the Baltic declined as a result of oil pollution (Lemmetyinen, 1966; Vermeer and Vermeer, 1975; Clark, 1984; vs. Joensen and Hansen, 1977). In the cases of two of the largest recent spills, the *Exxon Valdez* spill in Prince William Sound, Alaska and the Persian Gulf War (Box 5-4) release of oil in the northern Arabian Sea, the population-level impacts on seabirds are not clear.

There has been considerable variability in the estimates of the number of seabirds killed in the 1989 *Exxon Valdez* oil spill, which has led to much contention (e.g., Piatt and Lensink, 1989; Parrish and Boersma, 1995a,b; Piatt, 1995; Wiens et al., 1995, 1996; Ford et al., 1996, Piatt and Ford, 1996; Wiens et al., 1996; Day et al., 1997; Murphy et al., 1997; Lance et al., 2001). Piatt et al. (1990) provided an initial estimate that the number of seabirds killed in the spill was on the order of 100,000 to 300,000 birds (Piatt et al., 1990), and later, Piatt and Ford (1996) provided a best estimate of 250,000 birds killed. Even more difficult has been the determination of population-level impacts. Irons (1996) obtained evidence of lower rates of production of young in the surface-foraging black-legged kittiwake (*Rissa tridactyla*), but this did not translate into a decrease in the size of colonies in Prince William Sound, or even in the oiled portion of the Sound. The Common Murre (*Urea aalge*) was the species that sustained the highest mortality (Piatt and Anderson, 1996; Piatt and Ford, 1996), and it might have been expected that a population-level effect of this mortality

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BOX 5-4

Gulf War Spill, Arabian Gulf

Over a period of about four months from January-March 1991, crude oil was released into the Arabian Gulf from five tankers, a major tank field, and several offshore terminals, refineries, and battle-damaged tankers as part of the Iraq-Kuwait conflict. Though the actual volume of release will never be known, the best estimate is about 1,770,000 tonnes (520,000,000 gallons) (Tawfiq and Olsen, 1993), making it the largest oil spill in history and three times as large as the next largest spill (the 1979 Ixtoc well blowout in the Gulf of Mexico). Although the massive slicks were initially predicted to spread throughout the Arabian Gulf and out through the Gulf of Hormuz, a seasonal shift in wind patterns held the bulk of the oil along the shoreline between the Kuwait border and Abu Ali Island near Al Jubail, a distance of about 175 km. The oil fate was estimated by Tawfiq and Olsen (1993) as follows: 40 percent evaporated; 10 percent dissolved/dispersed; 10 percent recovered in Saudi Arabia; 15 percent stranded on shore in Saudi Arabia; and 25 percent unaccounted for. There was concern that a significant portion of the unaccounted for oil sank; however, Michel et al. (1993) did not find evidence for any significant sunken oil in the nearshore subtidal zone during diving surveys (197 dives) offshore the most heavily oiled shorelines and bays in Saudi Arabia. None of the researchers studying the Arabian Gulf after the spill reported large-scale oil contamination of bottom sediments (Price and Robinson, 1993).

The spill significantly affected shoreline habitats, with 707 km of shoreline oiled in Saudi Arabia alone, including 124 km of marshes (Gundlach et al., 1993). Very little shoreline cleanup was attempted. An estimated 50-100 percent of the intertidal biota were killed (Jones et al., 1996); in heavily oiled marshes, less than 1 percent of the plants survived (Böer and Warnken, 1996). Followup shoreline surveys in 1992 and 1993 showed that the stranded oil had penetrated up to 40 cm into the sediments, with liquid oil filling burrows in muddy sediments (Hayes et al., 1995). The heavy surface oiling formed persistent pavements along the upper intertidal zone and on the tops of mid-tide bars that showed little evidence of erosion six years after the spill. The surface pavements slowed the rate of subsurface oil weathering and physical removal, effectively sealing the subsurface oil in place. Intertidal species diversity in the lower intertidal zone on sandy and muddy substrates was 50-100 percent of controls by 1994, whereas in the upper intertidal zone, species density and density was 0-70 percent of unpolluted sites (Jones et al., 1996). As of 1997, there was little evidence of recovery of heavily oiled marshes. Much of the heavily oiled shoreline occurred along sheltered bays with little exposure to waves and currents. Thus, natural removal of the stranded oil will be very slow, and full recovery of intertidal communities will likely require decades.

Amazingly, no significant long-term impacts to subtidal habitats and communities were observed, including seagrass beds, coral patch and fringing reefs, unvegetated sandy and silty substrates, and rocky outcrops (Kenworthy et al., 1993; Richmond, 1996). Kuwait crude forms a very stable emulsion that resulted in thick surface slicks that stranded onshore rather than mixed into the water column. Impacts to shrimp stocks, however, were severe; in 1992 spawning biomass dropped to 1 percent and total biomass dropped to 27 percent of pre-war levels (Matthews et al., 1993). Causes of this collapse were attributed to a combination of mass mortality of eggs, larvae, and postlarvae resulting from oil exposure during the entire spawning season, emigration of adults out of the oiled areas, mortality of adults, heavy fishing of adults and juveniles thus further reducing the spawning biomass, and decrease in water temperatures and light intensity because of oil fires smoke and haze.

At least 30,000 seabirds are estimated to have died as a result of the spill. Although the oil spill killed an estimated 25 percent of the 1991 Saudi Arabian breeding population of the endemic Socotra cormorant, these colonies tripled in population by 1995 (Symens and Werner, 1996). Internationally important breeding tern populations in Saudi Arabia and Kuwait escaped direct oiling impacts in 1991 (70,000 pairs breed on offshore islands in summer), but severe declines in breeding success in 1992 and 1993 resulted from an acute shortage of food that was attributed to the oil impacts on fish recruitment (Symens and Alsuhaibany, 1996). In 1994, breeding success was high. During the spill, shorebird populations were reduced by up to 97 percent; however, it is not known whether the birds avoided the noxious oil or were driven away by a lack of food and found good feeding areas elsewhere, became oiled and died, or died from starvation (Evans et al., 1993). The greatest shorebird impacts, however, were likely the indirect effects of long-term degradation of intertidal habitats and the loss of their food supply.

would be evidenced by striking changes in the numbers or reproductive performance of murres nesting in the oiled area. Natural variability and the precision of population estimates, however, complicated the determination of impact to Common Murres, and it remained impossible to assign, with certainty, the population-level effects of the spill in this species (Boersma et al., 1995; Piatt and Anderson, 1996). Erikson (1995) also reported no evidence of depressed numbers of murres attending colonies in 1991, as compared to historic data. A lack of up-to-date monitoring in the murre colonies prior to the spill exacerbated the difficulties attendant on determining the effects of the spill. In other species, there was little evidence of significant population-level damage from the spill (Kuletz, 1996; Oakley and Kuletz, 1996; Sharp et al., 1996). Controversy as to the magnitude and duration of the effects of the spill is ongoing (e.g., Irons et al., 2001; Wiens et al., 2001).

In addition, some studies have argued that other sources of PAH in both the east and west Prince William Sound, including vessel traffic and PAH from coal and possibly from oil seeps further south in the Gulf of Alaska, may play a role (Page et al., 1996, 1998, 1999). There has also been consid-

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erable controversy concerning changes in avian use of nearshore marine habitats within Prince William Sound that might indicate long-term depression of bird populations using these waters (Day et al., 1995, 1997; Wiens, 1995; Wiens et al., 1996; Irons et al., 2000; Lance et al., 2001). Some studies found that, within two years of the spill 23 of 42 species showed no evidence of negative impacts from the spill (e.g., Day et al., 1995), whereas other investigators (Irons et al., 2000) found negative effects in 6 of 14 taxa up to nine years after the spill (Table 5-1). Some of these differences reflect methodologies used, whereas others appear to be matters of interpretation (Day et al., 1997; Murphy et al., 1997; Peterson, 2001). Effects differed between avian species that were apparently chronically exposed to oil residues through their epibenthic prey. For example, in surveys of habitat use by Barrow's Goldeneye (*Bucephala islandica*) in 1995, 1996 and 1997, Esler et al. (2000b) were unable to detect a significant effect of oiling history on habitat use, even though concurrent studies (Trust et al., 2000) found elevated levels of the enzyme cytochrome P450 1A in these birds, thus indicating on-going ingestion of oil-contaminated prey. Trust et al. (2000) also found elevated levels of cytochrome P450 1A in Harlequin Ducks (*Histrionicus histrionicus*) in oiled areas of Prince William Sound. In contrast to Barrow's Goldeneye, between 1995 and 1998, Harlequin Ducks within oiled areas of the Sound had lower densities (Esler et al., 2000a) and lower over-winter survival than did individuals over-wintering in non-oiled areas of the Sound. A demographic model suggested that the differences in over-winter survival between oiled and unoiled areas was sufficient to account for continued declines in the populations of Harlequin Ducks in the oiled areas. These effects reflect loss of individuals from habitually used wintering or foraging sites. Since it is unclear how these local "subpopulations" relate to biologically defined populations (stocks in fisheries parlance), it remains difficult to assess the "population" effects of this damage.

Wiens et al. (2001), using canonical correspondence analyses, found that although there was a clear effect of the spill, in years subsequent to the spill there was increasing occupancy of previously oiled sites by all species that had exhibited initial spill impacts. However, all species recovered at the same rate, so community composition was affected over time, though the consequences of these effects are unknown.

It is also less than clear that the immense discharges of petroleum into the marine environment during the Persian Gulf War in 1991 had a lasting effect on the populations of seabirds breeding in the northern Arabian Gulf (Case History 5-3). For example, during the war, an estimated 8,000 to 10,000 Socotra Cormorants (*Phalacrocorax nigrogularis*) were killed, approximately 50 percent of the Saudi Arabian population (Symens and Werner, 1996). As of 1995, the population had rebounded to 30,000 pairs, suggesting that the losses to oil during the war had little population-level effect, except possibly in slowing the rate of post-war increase. In contrast, four species of terns nesting on the offshore islands of the northern Gulf of Arabia showed little evidence of oiling during 1991. Although about 1 percent of the total adult tern population was moderately to heavily

TABLE 5-1 Indirect, chronic, or delayed responses of birds to the *Exxon Valdez* oil spill (after Peterson, 2001)

Species	Foraging Ecology	Type of Response	Period/Duration	References
Black Oystercatcher	Intertidal invertebrates	Numbers declined post 1989	1990, with recovery by 1993	Klosiewski and Laing, 1994
		Chicks fed oiled mussels required more food for less growth and fledged later	1990 only	Andres, 1996, 1997
		Laid fewer eggs on renesting	1990 only	Andres, 1996, 1997
		Nesting disrupted on oiled island as compared to unoiled island	Recovery by 1993	Sharp et al., 1996
Harlequin Duck	Shallow sub-tidal invertebrates	Lack of recovery in numbers present in oiled areas	Not until at least 1991	Klosiewski and Laing, 1994; Day et al., 1995, 1997; Irons et al., 2000
		Decline in winter counts in western (oiled) vs. eastern (unoiled) Sound	Through 1997-1998	Rosenberg and Petrula, 1998; Rosenberg, 1999
		P450 1A induction	Tested for in 1998	
Barrow's Goldeneye	Shallow sub-tidal invertebrates, mussels	Declining numbers in oiled vs. unoiled areas	Through 1998	Holland-Bartels et al., 1999; Irons et al., 2000
		Elevated P450 1A levels	1996-1997	Trust et al., 2000
Cormorants, black-legged kittiwakes, murres, pigeon guillemot, mergansers, and loon	Shallow subtidal fishes	Continued depression in census counts along oiled shores vs. expectation	Through 1998 (except for 1993 for loons)	Irons et al., 2000

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oiled, less than 25 percent of the average of the <10 adult terns found dead each year between 1991 and 1994 were oiled (Symens and Alsuhaibany, 1996). Oiling apparently occurred when terns encountered tar balls while plunge diving in pursuit of small fish. Small spots of oil transferred from adults to eggs caused no decline in hatching success (Symens and Alsuhaibany, 1996). There was evidence that the oil spilled during the Persian Gulf War had an indirect effect on tern reproductive success. The clutch sizes of the White-cheeked Tern (*Sterna repressa*) were reduced in 1992 and 1993, and the breeding success (chicks per pair) of Lesser Crested Terns (*Sterna bengalensis*), White-cheeked Terns and Bridled Terns (*Sterna anaethetus*) were less in 1992 and 1993 than those in either 1991 or 1994. This decline in 1992 and 1993 was apparently caused by a lack of small fish on which to forage. Exposure to the massive spills during the Persian Gulf War significantly reduced the abundance of fish eggs and larvae (McCain and Hassan, 1993); Symens and Alsuhaibany (1996) suggest that this mortality of forage fishes resulted in a scarcity of fish prey for the terns in 1992 and 1993. In those two years, the diets of the terns shifted, and one of the larger species, the Swift Tern (*Sterna bergii*), resorted to eating the chicks of the smaller White-cheeked Terns, and stealing food from Lesser Crested Terns returning to their colonies. Although this example shows effects of an oil spill on the reproductive ecology of marine birds up to two years after the spill, Symens and Alsuhaibany (1996) suggested that this two-year interruption would have a negligible effect on the population biology of these long-lived seabirds.

Among marine mammals, river otters (*Lutra lutra*) in the British Isles and Alaska, and sea otters (*Enhydra lutris*) and harbor seals (*Phoca vitulina*) in Prince William Sound, Alaska, all showed short-term population declines after oiling of their inshore marine habitats (Baker et al., 1981; Spraker et al., 1994; Monson et al., 2000; Peterson, 2001). For some species, these effects may have persisted over ten years (e.g., sea otters, Monson et al., 2000). However, in the case of the *Exxon Valdez* oil spill in Prince William Sound, Alaska, considerable controversy remains concerning the magnitude of the initial losses and the duration of population-level effects (e.g., Garshelis and Johnson, 1995; Hoover-Miller et al., 2001). These uncertainties stem from the lack of sufficient pre-spill data to characterize the population status of these species and difficulties in obtaining adequate post-spill data to distinguish between local movements of animals and area-wide population effects.

Chronic or delayed responses of marine bird and mammal populations to petroleum hydrocarbons in the sea can occur because of continued ingestion of oil via contaminated prey, or because of failure of prey populations to recover subsequent to injury. In the 10 years since the *Exxon Valdez* oil spill, several species of birds and marine mammals have demonstrated indirect or delayed responses to the spill. These responses were found in sea ducks and shorebirds, species

PHOTO 23 Spills from coastal facilities such as marine terminals and tank farms make up nearly one quarter of the spills (by volume) associated with the transportation of petroleum. (Photo courtesy of Environmental Research Consulting.)

that forage primarily on intertidal and shallow subtidal invertebrates, as well as in several species that forage on small fish caught in inshore waters (Peterson, 2001). Seabird responses were of three types: reduced use of oiled habitats as compared to use of unoiled habitats for up to nine years post-spill, reduced numbers post-spill as compared to pre-spill, and lower growth and delayed fledging in a species that fed contaminated mussels to its young. Species of ducks with populations that continued to decline post-spill (Harlequin Ducks and Barrow's Goldeneye) both feed on shallow-water invertebrates, including mussels, and both showed elevated levels of the enzyme cytochrome P450 1A, indicating continued ingestion of petroleum hydrocarbons (Trust et al., 2000).

Marine mammal populations that may have exhibited prolonged effects subsequent to an oil spill include sea otter and harbor seal populations in Prince William Sound (Garshelis and Johnson, 1995; Hoover-Miller et al., 2001; Peterson, 2001). In some regions of the Prince William Sound, sea otter abundance had not recovered as of 1998 (Dean et al., 2000), whereas in other areas, sea otter numbers were as high or

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higher than prespill counts (Garshelis and Johnson, 1993). Other results indicating damage to otters that persisted for more than several years include the finding that the over-wintering mortality of juveniles was higher at oiled as compared to unoiled sites in the winters of 1990-91 and 1992-93 (Monson et al., 2000), and that mortality of prime-aged sea otters was higher than normal after the spill (Monson et al., 2000). The presumed cause of the failure of the sea otter population to recover is continued contamination via their prey. Some of the measured increases or decreases in sea otter populations may have resulted from local movements of otters or other behavioral or demographic phenomena, and assessment of long-term population effects of the oil spill to sea otters remains difficult and controversial. In the case of harbor seals, there is some controversy as to whether they have declined in Prince William Sound (Peterson, 2001), or whether the apparent declines are the result of movement of seals that were avoiding or moving away from oil contaminated haulout (Hoover-Miller et al., 2001). Harbor seals were declining before the spill, and if there has been a continued decline, it may be a continuation of the past decline, or it may be the result of a decrease in the abundance of near-shore fish prey, but the available evidence is inconclusive (Peterson 2001). What is important here is that sub-lethal effects can be identified in marine birds and mammals for several years after the acute effects of a spill have passed.

In summary, it has proven difficult, except in a few notable exceptions, to demonstrate population-level effects of oil spills for either marine birds or marine mammals based on censuses. Although many individuals may be killed, it is frequently difficult to demonstrate commensurate declines in local or regional populations, or to show significant demographic effects, because the power of present techniques to detect change is weak. Without more complete knowledge of the structure of populations of marine birds and mammals and their demography, it may remain beyond our reach to assign damage or recovery except in cases where ongoing monitoring provides an adequate basis for comparative studies. The temporal and spatial variability found in ecosystems makes even the most sophisticated statistical approaches open to individual interpretation and controversy (Wiens and Parker, 1995; Day et al., 1997; Irons et al., 2000; Peterson, 2001). As both Nisbet (1994) and Piatt and Anderson (1996) point out, even though we often cannot demonstrate statistically that oil pollution has caused population-level effects in marine birds, given what we know of their life history patterns, including long life spans, low adult mortality, and low rates of reproduction, it is risky to assume that increased rates of mortality are without population-level effect. Total population size, including breeders and non-breeders, has not been determined for any seabird species, and thus it is impossible to determine directly whether pollution is affecting global populations (Nisbet, 1994). Only if the effects of oil pollution are compensatory and not additive to other, natural, causes of mortality can we hope that large removals of individuals are without population-level consequences. The same arguments should hold true for marine mammals.

Modeling the Impacts of Oil

Modeling has been used in many ways to assess the impacts of oil spills on living resources and habitats:

- To evaluate the impacts of an oil spill using a model, the fate of the oil must first be quantified. Historically, most oil fate models have focused on the trajectory and fate of oil on the water's surface (e.g., see reviews by Huang and Monastero, 1982; Spaulding, 1995; ASCE, 1996; Reed et al., 1999). Surface trajectory models are used to calculate the intersection of the trajectory path with maps of resources of concern including biota and habitats (e.g., Samuels and Lanfear, 1982; Seip et al., 1991). This approach is appropriate for quantification of impacts to birds, mammals, and shoreline habitats. Bird and mammal impacts have also been modeled by backtracking from locations where oiled animals have stranded on beaches, accounting for losses at sea (Seip et al., 1991; Ford et al., 1996).
- To evaluate the effects of subsurface oil, subsurface oil must be explicitly tracked (French et al., 1996, 1999). A prime example is the North Cape oil spill of January 1996 that occurred during a severe winter storm (French, 1998a,b,c) (Case History, 4-1).
- To evaluate impacts on aquatic biota, oil entrainment and dissolution into the water must be simulated. The relevant concentrations are of those components that might have an impact on aquatic organisms and habitats. The concentrations of main concern are the soluble and volatile lower- and intermediate-molecular-weight compounds that are acutely toxic to biota, primarily monoaromatic hydrocarbons (MAHs) and polycyclic aromatic hydrocarbons (PAH) (French, 2000; French McCay, 2001). Other compounds in oil may also contribute to toxicity. Submerged oil and oil smothering on shorelines are also important exposure pathways. Thus, the model must consider the entire fate of the oil and all its components over time, both on and in the water, and in sediments.

Modeling Impacts of Oil on Shoreline Habitats

Oil trajectory models have been used to determine where oil will intersect the shoreline and impacts are presumed if oil reaches a location. The problem with this approach is that impacts are related to the amount and weathering state of the oil. Thus, this simply identifies areas that might be exposed to some amount of oil, but does not quantify an impact.

Computer models of the physical fates, biological effects, and economic damages resulting from releases of oil and

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other hazardous materials were developed for use in Natural Resource Damage Assessments (NRDA) under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) and the Oil Pollution Act of 1990 (OPA) (French and French, 1989; Reed et al., 1989; French and Reed, 1991; French, 1991; French et al., 1996; Reed et al., 1996). There are presently two models in regulation: the Natural Resource Damage Assessment Model for Coastal and Marine Environments (NRDAM/CME, French et al., 1996) and the Natural Resource Damage Assessment Model for Great Lakes Environments (NRDAM/GLE, Reed et al., 1996).

The NRDA models simulate spreading and shoreline stranding of oil. The amount of oil remaining on the shoreline is a function of oil viscosity and shoreline type. Stranded oil is assumed to be removed by waves and other physical processes at a constant rate. The holding capacities and removal rates are based on data collected after spills. Impacts on intertidal habitats, such as salt marshes, mangroves, macroalgal beds and coral reefs, are assumed to be a 100 percent loss if a threshold thickness (dose) is exceeded for any interval of time. The threshold is based on observational data for salt marsh impacts (French et al., 1996).

Modeling Impacts of Surface Oil to Wildlife

Wildlife (birds, mammals, and reptiles) are primarily impacted by direct exposure to floating oil, ingestion of contaminated prey or depletion of food resources. Impacts via a loss of food resources are included in the NRDAM/CME (French et al., 1996), under the assumption that wildlife are food-limited and a proportionate loss of wildlife biomass would result from lost prey production because of a spill. Models used to assess impacts of oil on wildlife populations are summarized in Table 5-2.

In evaluating the wildlife impacts of the *Exxon Valdez*, Ford et al. (1996) used experimental bird drift and loss rates to estimate the percent of oiled animals that would reach a beach and be stranded. Oiled and dead birds are scavenged and may sink at sea. The percent stranded is related to the trajectory of the carcasses. Ford et al. (1996) used reverse trajectory modeling to determine where beached animals originated, and the percent loss estimates from the drift experiments, to estimate a total kill.

In the NRDAM/CME (French and French, 1989; French et al., 1996), wildlife, oiled and killed, are a function of area swept by surface oil, dosage, and vulnerability. Wildlife are assumed to move randomly within the habitats they normally use for foraging. The dose is estimated from the oil thickness, path length through the oil, and the width of a (swimming) bird. A portion of wildlife in the area swept by the slick is assumed to die based on the probability of encounter with the slick, dosage, and mortality once oiled. Estimates for these probabilities are derived from information on behavior and field observations of mortality after oil spills.

French and Rines (1997) performed hind-casts on 27 oil spills to validate the wildlife impact model. The results showed that the model is capable of hind-casting the oil trajectory and shoreline oiling, given (1) accurate observed wind data following the spill, and (2) a reasonable depiction of surface currents. Since winds and currents are the primary forcing variables on oil fate, obtaining accurate data on these is very important to the accuracy of any simulation. The accuracy of the impact model is primarily dependent on the accuracy of the wildlife abundance data for the time and location of the event. In the validation study, regional mean abundances from literature sources were assumed.

In nearly all cases, impact information for a spill consists primarily of counts of rescued or dead wildlife. Model validation is necessary to illustrate where the model predicts reasonable estimates of impacts on wildlife. Modeling results show that the wildlife impact algorithm in the model is valid when input data on abundance are accurate (French and Rines, 1997). In a few cases, the model estimated more birds killed than were observed. These cases were for species impacts not normally assessed or reported. Even in cases where large efforts were made to recover oiled wildlife, such as following the *Exxon Valdez*, it is well recognized that many oiled animals are lost at sea or scavenged and not counted directly as oiled. Small and less visible species and

TABLE 5-2 Models Used to Assess Impacts of Oil on Wildlife

Purpose	Reference
Sea birds—Oil spill trajectory model and oil vulnerability index	Samuels and Lanfear, 1982
California sea otter—Sea otter movements and oil spill trajectory model	Brody, 1988
Sea birds and marine mammals—Oil slick encounter and subsequent mortality	Ford et al., 1982; Ford, 1985
Gray and bowhead whales—Oil spill impacts	Reed et al., 1987a; Jayko et al., 1990
Fur seal model—Simulated population processes and mortality due to oiling	Reed et al., 1987b; French et al., 1989; Reed et al., 1989
Sea birds—Estimate numbers oiled from strandings of oiled animals on beaches	Seip et al., 1991; Ford, 1987; Ford et al., 1996
Exxon Valdez—Experimental bird drift and loss rates to estimate the percent of oiled animals that would reach a beach and be stranded.	Ford et al., 1996

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those that remain at sea will be the most under-counted. Thus, it is not possible to verify some of the model estimates of impacts. The model results point to where additional observations are needed to evaluate impacts to these less obvious species (French and Rines, 1997).

Modeling Impacts of Subsurface Oil on Aquatic Biota

Oil toxicity models have been developed to estimate water column toxicity after an oil spill (French, 2000; French McCay, 2001). As discussed above oil toxicity may be attributed to many different compounds. Exposure concentrations of each compound in the mixture, as well as their toxicities, must be estimated to quantify the toxicity of oil to water column organisms (French et al., 1996; Anderson et al., 1987; French, 2000; French McCay, 2001). Typically, for surface releases of fuel and crude oils, only the PAH are dissolved in sufficient quantity and remain in the water long enough for their toxic effects to be significant. The more turbulent the release (i.e., if it is during a storm or from a blowout or pipeline under pressure), the higher the relative concentrations of the more toxic PAH, and the higher the impacts to water column organisms. For a subsurface release deep in the water column or for a gasoline or other product spill where the MAHs and lower molecular weight aliphatics are significant fractions of the oil, all of these compounds may cause significant acute toxic effects (French, 2000; French McCay, 2001).

The biological model in the NRDAM/CME (French et al., 1996), and the updated version of that model, SIMAP (French et al., 1999), which includes the oil toxicity model described above, estimates acute toxic response of aquatic biota. (Because of the widespread use of SIMAP, the approach it represents is fairly widely known. Other, less familiar models may address the challenges of modeling oil spill fates and effects at least as well.) Fish and their eggs and larvae are affected by dissolved contaminant concentration (in the water or sediment). Mortality is calculated using LC_{50}, corrected for temperature and duration of exposure, and assuming a log-normal relationship between percent mortality and dissolved concentration. Movements of biota, either active or by current transport, are accounted for in determining concentration and duration of exposure. Organisms killed are integrated over space and time by habitat type to calculate a total kill. Lost production of plants and animals at the base of the food chain is also computed. Lost production of fish, shellfish, birds, and mammals due to reduction or contamination of food supply is estimated using a simple food web model (French et al., 1996). In addition to the direct kill and food-web losses of eggs and larvae, young-of-the-year fish may be lost via habitat disruption. This is included in the model for wetland and other nursery habitats destroyed by lethal concentrations or oiling. Losses are related to the habitat loss. Thus, recovery of spawning and nursery habitat in wetlands follows recovery of plant biomass and production (French et al., 1996).

Applicability of Modeling

Success of a model simulation is dependent on both the algorithms and the accuracy of the input data. Results of the validation exercises have shown the algorithms provide reasonably accurate results. The most important input data in determining accuracy of results are winds, currents, and biological abundance of the affected species. These data inputs need to be site- and event-specific for an accurate model estimate of impacts of a spill. Thus, the limitations of modeling are largely driven by the availability of these input data (French and Rines, 1997; French, 1998a,b,c).

While oiled wildlife and shoreline habitats may be observed and quantified in the field after a spill, it is difficult and often infeasible to measure directly impacts to aquatic biota in the water column. To characterize fully the impact by field sampling, water and sediment samples would be needed at frequent time intervals over the first few weeks after the release (and especially in the first 24-48 hours), and with enough spatial coverage to characterize the extent of contamination. In addition, comprehensive sampling of each of the species affected is needed in the exposed and unaffected areas. Because marine organisms are patchy in their distribution, large numbers of stations and samples within stations are needed to map abundance accurately. Such extensive sampling of all (or even selected) species affected is often not feasible, given the rapidity at which the evidence disappears (by scavenging of killed organisms and by migration of animals into the impacted area). Modeling may be used in combination with field sampling to quantify oil fate and impacts (French, 1998a,b,c).

The weaknesses of modeling are related to our incomplete scientific knowledge of the impacts of oil spills. Because oil spills are infrequent and unplanned events, which have most of their effects on organisms over a very short time, it is very difficult to obtain quantitative information with which to develop and verify models. The implementation of NRDA regulations under OPA has facilitated the gathering of quantitative data on spills, and provided opportunities for improving and verifying models.

Effects on Communities and Habitats

Effects on communities will be discussed from the standpoint of habitat types in which they occur. Two broad habitat categories are considered: (1) biogenically-structured habitats, and (2) inorganic substrates, such as intertidal rock, sand, and subtidal muds.

Biogenically-structured Communities

Long-term and chronic effects are likely to be expressed as residual damage from oil spills to biogenically-structured communities, such as coastal wetlands, reefs, and vegetation beds. Effects of oiling on biogenically-structured habitats may result from acute damage on habitats such as coral

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reefs, live-bottom habitats, mangrove swamps, salt marshes, oyster reefs, and seagrass and kelp beds. Here the concern is that even though oil may not persist following an oil spill, the time required for recovery of damaged populations of organisms that provide the physical structure of the habitat may be many years. In some biogenic habitats, such as mangroves and mussel beds, oil can sometimes penetrate into the lower-energy sediments associated with these habitats and have potentially long-lasting effects. Biological communities that are integrally dependent on physical structures, which are themselves formed by living organisms, may be inherently slow to recover from severe impacts. In some cases where the structure-forming species actually stabilize the habitat, it is conceivable that permanent modification of that habitat could result from an acute incident that kills the key structuring species. Recovery from the effects of an oil spill in a community in which organisms provide the physical structure of the habitat depends on structural damage incurred during cleanup operations, the persistence of contamination, and the inherent ability of the community to recover.

Corals

The 1985 Oil in the Sea report focused extensively on the effects of oil spills on tropical habitats including coral reef ecosystems and mangroves. At the time, there were multiple field studies documenting effects on corals including decreased feeding response, coral colonization and premature expulsion of coral planula. The end result was coral tissue death, coral bleaching, and the loss of an entire year's larval recruitment class. One lament of the 1985 Oil in the Sea report was the lack of information on concentrations and composition of oil in the water that prevented comparison of spill effects between coral sites.

Since 1985, a wealth of field and laboratory studies have increased our knowledge of the effects of oil on coral reefs. The 1986 Galeta spill into Bahia las Minas, Panama is arguably the most studied oil spill in the tropics. Large amounts of medium weight crude oil (see Box 5-5) spilled into mangroves, seagrass beds, and coral reefs on the Caribbean coast of Panama (Burns and Knap, 1989; Jackson et al., 1989; Guzman and Holst, 1993; Guzman et al., 1994; Box 5-5). Another notable tropical oil spill was the consequence of the Persian Gulf War in 1991 where 1,770,000 tonnes of oil were spilled into the marine environment (Price and Robinson, 1993). Despite a 120-fold difference in total volume of oil spilled, the long-term effects (greater than five years) of oil in Panama were more pronounced and detrimental due likely to repeat inoculation of oil from the surrounding mangroves into the coral ecosystem. In contrast, no long-lasting effects to the coral reef ecosystem were reported from the Persian Gulf War spills (Price and Robinson, 1993).

Corals located in intertidal reef flats are exposed to oil slicks and are more susceptible to damage and death than corals in subtidal reefs. Coral located subtidally or in areas with high wave action are not directly exposed to the marine surface layer where oil slicks can coat them. Instead, only the water-soluble fraction of oil generally affects submerged coral. The water-soluble fraction is primarily composed of benzene, toluene, ethylbenzene, and xylene, which can rapidly evaporate to the atmosphere. One laboratory study found that 15 percent of the benzene and toluene and 80 percent of the xylene were lost after 24 hours of exposure to the atmosphere (Michel and Fitt, 1984).

Acute and chronic exposures of oil on coral have been studied in the laboratory and field (reviewed by Peters et al, 1997). The symbiotic algae associated with coral are affected after 24 hours of exposure to the water-soluble fraction of oil (benzene, toluene, ethylbenzene, and xylene; see Box 5-2). Photosynthetic capacity can recover fully if there is only short-term exposure to oil (less than 72 hours), and no adverse affects were measured for exposure of less than one hour (Michel and Fitt, 1984). Mixtures of dispersants and oil are more toxic to coral than just the oil (Peters et al, 1997). Branching coral (e.g., *Acropora palmata*) is considered more sensitive to oil exposure than massive coral (e.g. *Montastre*, Bak, 1987).

Mussels

Mussels often occur in dense intertidal aggregations and their interlocking byssal threads provide a low-energy habitat with protection from the rigors of breaking waves above the bed. The interstices of mussel beds are micro-habitats rich in intertidal life (Ricketts and Calvin, 1948). As with other bivalves, mussels effectively accumulate high concentrations of a variety of contaminants including petroleum hydrocarbons from the water and their food.

Mussels can be affected by the accumulation of petroleum compounds. Low concentrations of petroleum hydrocarbons can interfere with cellular and physiological processes like cellular immunity (McCormick-Ray, 1987; Dyrynda et al., 1997), lysosome characteristics (Pelletier et al., 1991), byssus attachment (Linden et al., 1980), growth (Widdows et al., 1987, 1989), and ability to tolerate air exposure (Thomas et al., 1999). Thus, there is a basis for expecting population impact under some conditions. Oil exposure or vigorous cleanup of the intertidal zone results in damage to these beds, and it may take years for the beds to re-establish their former richness. At the same time mussel beds effectively trap oil and under some circumstances allow the oil to persist for years after a spill. For example, after a 7,000 tonnes spill into a tropical estuary with mangrove habitats, damage to mussels was apparent one year after the spill (Garrity and Levings, 1993). A spill of Bunker C fuel oil, spilled from a collision of two tankers in San Francisco Bay in 1971, resulted initially in smothering of intertidal invertebrates. Five years after the spill, there was no evidence of long-lasting effects of the oil spill on recruitment patterns of intertidal invertebrates in high energy environments (Chan, 1977).

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BOX 5-5

Galeta Tank Spill, Bahia Las Minas, Panama

On April 27, 1986 a storage tank at a refinery at Bahia Las Minas, Panama ruptured, releasing an estimated 14,300 tonnes (4,200,000 gallons) of a blend of 70 percent Venezuelan and 30 percent Mexican crude oil (API gravity = 27) into the sea (Keller and Jackson, 1993). Onshore winds kept the oil trapped in deep bays near the release site for six days, but shifting winds and rainfall runoff caused the slicks to spread to adjacent areas. Dispersants were applied (21,000 L) starting nine days after the spill. Eventual impacts resulting from dispersant application could not be separated out from other factors.

About 82 km of coastline were heavily oiled, including more than 1,000 ha of mangrove forests, intertidal reef flats, and subtidal flats and seagrass beds. These habitats received extremely heavy dosing of a medium-heavy crude oil. There was some shoreline cleanup on beaches and rocky shores, and channels were dug into mangroves in an effort to increase oil flushing from interior areas. Large expanses of mangrove forest were inaccessible, however, and no oil removal was conducted there. Approximately 69 ha of mangrove forest (dominated by the red mangrove, *Rhizophora mangle*) were killed; sublethal impacts affected approximately 308 ha (Duke et al., 1997).

The spill affected a biological preserve at the Smithsonian Tropical Research Institute, where biological baseline studies had been conducted since 1970, sixteen years pre-spill. Because of these extensive baseline data, the U.S. Minerals Management Service funded studies of the fate and effect of the oil in this tropical ecosystem for five years (Keller and Jackson, 1993); many important findings have resulted. Oil in surficial soils degraded within six months; however, pools of oil trapped in mangrove soils showed little degradation, and chronic re-oiling of adjacent areas occurred for at least five years (Burns et al., 1994). Oil concentrations in bivalves were 5-15 times background five years post-spill, with seasonal highs associated with periods of oil remobilization. The mangrove fringe along the outer coast, lagoons, and tidal creeks was frequently re-oiled, resulting in high prop root mortality and severe impacts on attached populations and communities that was most severe five years later (Garrity et al., 1994).

Where the oil floated over the reef flats, there was little mortality. The spill occurred, however, during a period of low tides, and oil was trapped on the seaward borders of the reef flat. Wherever the reef flat was in direct contact with the oil, there was extensive mortality, and the effects persisted for over five years for sessile species (Cubit and Connor, 1993). Mortality to intertidal communities and organisms was not a widespread, toxic effect of oil mixed in water, because the oil had weathered prior to stranding. A primary factor in the recovery rate for sessile biota on reef flats was also how much of the plants and animals survived the spill and cleanup, and then vegetatively spread or washed in from nearby habitats afterwards—an important factor in cleanup design.

In most areas, subtidal seagrass beds (*Thalassia*) showed sublethal impacts but recovered within eight months. The exception was the shoreward margins of the beds that died off in a band 20-90 cm wide. The fauna of oiled seagrass beds remained highly altered for 2-3 years post-spill (Marshall et al., 1993). As mangrove forest and seagrass beds died back, oiled sediments were exposed and eroded, providing a chronic source of oiled sediment for re-deposition in adjacent habitats. Subtidal reef corals (*Diplora clivosa*, *Porites asteroides*, and *Siderastrea siderea*) were affected to water depths of 6m, with a strong correlation between effects and oil concentrations in subtidal sediments (Guzman et al., 1993). Affected coral populations had not started recovery after five years, as demonstrated by reduced sexual reproduction and larval recruitment, reduced populations of grazing fish, and very low recruitment of most formerly dominant coral species. Minimal estimates of the time required for equivalent populations to become established were10-20 years (Guzman et al. 1993).

Studies among the habitats showed consistent patterns in recovery rates; that is, species with high reproductive potential, planktonic stages, and immigration or wave transport of fragments of surviving sessile species from adjacent habitats recovered more quickly, whereas those with low dispersal abilities and low reproductive potentials recovered more slowly. Habitats where heavily oiled sediments persisted or where they were exposed to chronic re-oiling also recovered slowly. This spill provided some of the best evidence of the complexity of the tradeoffs of natural recovery versus the impacts of cleanup in sensitive environments.

In the *Exxon Valdez* spill, mussel beds were contaminated with oil, and it was decided not to disturb the mussel beds during cleanup operations. This decision was based partly on the food value of mussels to sea ducks, shorebirds, and sea otters (A. Weiner, Alaska Department of Environmental Conservation, personal communication). As a consequence, oil persisted in these less energetic habitats within the intertidal zone. In these environments, oil was retained in the sediments underneath the mussel beds in an unweathered state for many years after the spill and would be expected to continue to persist (Babcock et al., 1997; Carls et al., 2001). There were at least 50 such mussel beds identified in western Prince William Sound, and it is likely that oil will only slowly decrease in these environments without intervention. Since it appears that some species of fish, sea birds and sea otters are still exposed to low levels of oil in western Prince Williams Sound 11 years after the spill, and some of the highest remaining concentrations of oil are found in mussel beds, these beds might be contributing to the continuing contamination of higher-trophic-level species (e.g., Duffy et al., 1996). Boehm et al. (1996) examined the distribution of PAH in mussels collected at various sites within Prince William Sound and observed wide spatial variation in PAH concentrations in mussels from different habitats and predicted that concentrations would fall to background levels within a few years. There is no consensus yet on which choice is best: immediate cleanup with destruction of mussel beds that may take many years to re-establish, or leaving them alone to

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naturally weather and risk uncertain effects at higher trophic levels over long periods.

Subtidal Vegetation

Studies of oil effects on sea grass (e.g., *Thalassia* sp., *Halophila* sp., *Zostera* sp.) are limited to short- and long-term effects from particular oil spills. Little evaluation of chronic or acute damage from laboratory studies exists. Eelgrass meadows in the tidal zone are generally directly exposed to oil and die-off in the first year of an oil spill. In the subtidal areas, damage is limited to dying leaves. After the initial mortality in the first year, long-term effects of eelgrass are mixed. Long term (> 5 years) effects at the *Exxon Valdez* spill were inferred by decreased mean density of shoots and flowering shoots in the oiled area. Biomass, however, was the same between oiled and non-oiled areas (Dean et al., 1998). In the Persian Gulf War spills, no difference between oiled or non-oiled seagrass meadows could be detected after one year (Kenworthy et al., 1993). Reasons for resilience of eelgrass are speculative but are likely a result of life history patterns. Some species such as *Zostera marina* in Alaska propagate by lateral root growth, not by producing germinating seeds, and are less susceptible to oil in the sediment. Environmental parameters such as time of year of the spill relative to germination may also be important, but remains unexplored.

Subtidal kelps are apparently not particularly vulnerable to petroleum hydrocarbons. Around shallow-water natural petroleum seeps, the large kelp *Macrocyctis pyrifera* (in the sporophyte stage) does not accumulate petroleum hydrocarbons to very high concentrations (Straughn, 1976), and these kelp beds are well-developed despite continual inundation with surface oil. Laboratory and field studies indicate that gametophytes of this species may be more sensitive than mature plants (Reed et al., 1994). Following the *Exxon Valdez* spill, some large subtidal kelps had different size distributions in oiled areas compared to non-oiled areas, but it is uncertain if this was a spill effect (Dean et al., 1996). In the *Nakhodka* oil spill in Japan, no effects on subtidal kelp were reported from field surveys (Hayashi et al., 2000).

Like mussels, which retain oil in their byssus threads, kelp holdfasts are also low-energy environments that can retain oil for years after a spill. For example, a small spill of diesel oil at Macquarie Island in the sub-Antarctic resulted in contamination of holdfasts of kelp that lasted for at least five years and inhibited the full recovery of the kelp-associated invertebrate community from the effects of the oil (Smith and Simpson, 1998).

Intertidal Vegetation

Estuaries in many areas of the world are susceptible to exposure by oil because of the location of petrochemical industries in the coastal zone and transport of oil products, either by vessel or via pipelines, that either pass closely by or through estuaries. Spills or operational discharges can potentially cause damage to intertidal vegetated habitats, including salt marshes and mangroves. These types of vegetation may occur separately or in combination with each other. Oil spills are known to cause severe and long-term damage to mangrove and salt marsh ecosystems (e.g., Teal et al., 1992; Burns et al., 1993; Duke et al., 1997; Mille et al., 1998). The vegetation and the structure that salt marshes and mangroves provide may be affected, sediments may be contaminated, and ecosystem functions may be impaired with regard to utilization by organisms, including important fisheries species, geochemical cycling, and stabilization of sediments. The rate of degradation of the oil in the sediments is influenced by the sediment type, oxygen content and bacterial community of the sediment, availability and level of nutrients in the sediments and at the oil/sediment interface, and the depth to which the oil has penetrated. Oiling effects may be limited or negligible and short-term when the oil exposure is minimal, the vegetative structure is not impacted (either by the oiling or various cleanup procedures), and residual oil levels are minimal or rapidly weathered. Oiling effects are particularly great when oil coats the vegetation or is incorporated deeply in the sediments beneath the vegetation.

Salt Marshes

The negative effects of oil on marsh vegetation are dependent on the type of oil (constituents, viscosity), the amount of oil, the amount of plant coverage, the depth of penetration of the oil into the marsh sediments, the season, and the type and effectiveness of any cleanup or remedial actions (reviewed by Webb, 1996; Pezeshki et al., 2000) (Table 5-3). Lighter and more refined oils such as No. 2 fuel oil are extremely toxic to smooth cordgrass (*Spartina alterniflora*). Crude oils and heavy fuel oils are generally the same in overall effects on plants, i.e., little toxic effects to plants occur unless the oil penetrates into the sediments and chronic toxicity to the plants occurs as roots are continuously exposed to oil. The aboveground portion of smooth cordgrass is generally killed only when oil covers all plant surfaces. Regrowth from roots will occur soon after death of the aboveground portions of the plants. If sediments are heavily contaminated by oil, then production of new shoots is problematic and plant recovery is diminished. Oil spills are more damaging to smooth cordgrass during the spring growing season than in fall when the plants are beginning their dormancy. Regrowth the following spring after a fall oil spill does not appear to be greatly reduced. Oil coverage of 1 to 2 l/m^2 was generally dispersed with the tides, leaving little to penetrate sediments and cause long-term damage. When high levels of crude and heavy fuel oils accumulate in the sediments or remain within the marsh for long periods, the result is complete death of large areas of smooth cordgrass.

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TABLE 5-3 Data from Field Studies on Impacts to Marsh Vegetation from Experimental, Single-dose Oiling (from Hoff et al., 1996)

Location	Vegetation	Oil Type	Time of Oiling	Cleanup	Recovery Time
Galveston Bay, Tex.[a]	*Spartina alterniflora*	Arabian crude	Nov.	none	1 yr
		Lybian crude			1 yr
		No. 6 fuel			1 yr
		No. 2 fuel			2 yr
Louisiana[b]	*Spartina alterniflora*	S. La. crude	June	none	3 mos
				flushing	3 mos
				cutting	2-5 yr
York River, Va.[c]	*Spartina alterniflora*	S. La. crude fresh/weathered	Sept.	none	
St. Louis Bay, Miss.[d]	*Juncus roemerianus*	Empire Mix crude	March	none	>1 yr
		Saudi crude			1-3yr

[a]Webb et al., 1985
[b]DeLaune et al., 1984
[c]Bender et al., 1977
[d]de la Cruz et al., 1981

In a series of experimentally oiled salt marsh plots, cleanup techniques implemented 18 to 24 h after the application were not effective in removing oil that had penetrated the surface (Kiesling et al., 1988). When oil remained on the sediment surface, flushing techniques were most effective at removal, reducing levels of oil by 73 to 83 percent. When dispersants were added to the water during flushing, oil removal was only slightly enhanced. Clipping of vegetation followed by sorbent pad application to sediments was moderately effective, reducing added oil by 36 to 44 percent. Burning had a negative effect on oil removal; oil increased in sediments of burned plots compared to controls. Consideration should be given to natural microbial breakdown of the oil that can be facilitated with fertilizers. When large amounts of oil are present on a marsh, damage from trampling during cleanup can be severe, causing damage to plants and forcing oil into the sediments (Webb, 1993).

Densities of animals in salt marshes may be reduced by acute, short-term toxic effects of crude oil that sharply increase mortality rates (Anderson et al., 1974; Sanders et al., 1980; McDonald et al., 1991; Nance, 1991; Widbom and Oviatt, 1994), or cause avoidance by mobile organisms (Moles et al., 1994). Oil may persist in marsh sediments for many years (Teal and Howarth, 1984; DeLaune et al., 1990; Teal et al., 1992) and may continue to affect habitat use. Populations of opportunistic infaunal organisms, such as capitellid and spionid polychaetes and nematodes, are often enhanced in oiled sediments if the concentrations are not high enough to be toxic (DeLaune et al., 1984; Rozas et al., 2000). Many of these organisms in highly urbanized estuaries and in estuaries near petrochemical installations or petroleum production facilities may be acclimated to hydrocarbons (Smith et al., 1984; Carman et al., 1995).

Chronic contamination was studied in marsh areas of upper Galveston Bay, Texas that receive episodic oil from spills in the San Jacinto River and the Houston Ship Channel (Rozas et al., 2000). Marsh sediments were contaminated with low levels of petroleum hydrocarbons, but there were few statistically significant negative relationships between animal density (fish and decapod crustaceans) and hydrocarbon concentration (Rozas et al., 2000). Further, hydrocarbon concentration was not important among the environmental variables measured in explaining animal densities. The conclusions of Rozas et al. (2000) were that background levels of weathered oil in marsh sediments did not affect habitat use by most estuarine organisms; however, they noted that the longer-term effects of continued exposure that might result in chronic, sublethal effects were not known. The background levels found in the Galveston Bay marshes were similar to those found in other highly urbanized estuaries (Overton et al., 1986; Bomboi and Hernandez, 1991). The low concentrations of weathered petroleum hydrocarbons in the Galveston Bay marsh study were one to two orders of magnitude lower than the average value of 2-5 mg/g (produced water versus oil) that Nance (1991) reported was needed to depress populations of benthic organisms in a small bayou connected to the Galveston Bay estuary. Even though oil may initially reduce the use of intertidal habitats by aquatic organisms (Sanders, 1978; Burns and Teal, 1979; Maccarone and Brzorad, 1995), habitat use may return to normal levels after the oil has undergone sufficient weathering (Barber et al., 1995).

One of the most detailed post-spill studies was carried out on the long-term effects of No. 2 fuel oil spilled in Buzzards Bay, Massachusetts that affected a 8-km stretch of salt marsh shoreline (Sanders et al., 1980). The oil had its greatest effect, and persisted the longest, in the Wild Harbor marsh (versus a control in Sippewissett marsh 4 km to the south). Marsh grasses contaminated with oil died. Recovery of the Wild Harbor marsh was well along five years after the spill,

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but probably not complete. The population of fiddler crabs in the Wild Harbor marsh was reduced relative to that in Sippewissett marsh for at least seven years (Krebs and Burns, 1977). Behavioral effects, abnormal burrow shapes, and reduced female-to-male ratios were seen in Wild Harbor. Crab density was negatively correlated with aromatic hydrocarbon concentrations within the marsh, as was the density of newly settled juveniles.

Other sources of oils that may directly affect salt marshes or mangroves are produced water discharges. Results from Louisiana estuaries indicate that discharges of produced waters directly onto salt marshes will kill the vegetation, but discharges into receiving waters do not affect the peripheral marsh vegetation (Boesch and Rabalais, 1989a). Within the Nueces Bay estuary of Texas, however, Caudle (1995) identified extensive marsh areas in the bay that were denuded of vegetation due to long-term exposure to produced water.

Documented recovery times (return to some precursor percent cover of vegetation, diversity, or height and biomass of plants) for oiled marshes range from a few weeks to decades (reviewed by Hoff, 1996). There are several well-studied marsh sites where recovery times ranged from five years to greater than 20 years, including two sites in Buzzard's Bay. Massachusetts, the *Miguasha* spill in Quebec, the *Metula* spill in Chile, and the *Amoco Cadiz* in France (Table 5-4). The reasons for longer recovery times were related to the following characteristics: (1) northern, temperate, cold environments, (2) the high organic content of the peaty soils, (3) sheltered location, (4) heavy oiling, (5) spills of fuel oils (bunker C or No. 2 fuel), and (6) physical disturbance during response activities, particularly for the *Amoco Cadiz*.

In contrast, recovery times of three years or less have been documented for sites at several locations in the Gulf of Mexico: Neches River, Texas (*Esso Bayway*), Harbor Island, Texas pipeline, and a pipeline rupture in southeastern Louisiana (Table 5-5). These marshes exhibiting quicker recovery share the following characteristics: (1) warm climate, (2) more mineral-rich soils, (3) light to moderate oiling, (4) spills of light to medium crude oil, and (5) variety of cleanup methods that were less intrusive. In many instances, cleanup techniques delayed recovery time, from physical disruption of roots, flushing of soils, thus lowering the soil surface below levels where vegetation could re-establish, and activities that mix oil deeper into the marsh soils.

Mangroves

There are numerous documentations of the death, defoliation, genetic, and other damage to mangroves and their associated communities after exposure to oil (e.g., Proffitt et al., 1995). Damage to mangrove forests varies with the amount and toxicity of the spilled oil product(s) with or with-

TABLE 5-4 Examples of Oil-impacted Marshes with Recovery Times of Five Years or More, Documented by Follow-up Studies (from Hoff et al., 1996).

Location	Vegetation	Oil Type	Time of Oiling	Cleanup	Recovery Time
Chile *Metula*[a]	*Salicornia ambigua* *Suaeda argentinensi*	Arabian crude Bunker C	Aug. 1974	none	> 20 yrs
Quebec *Miguasha*[b]	*Spartina alterniflora* *Spartina patens*	Bunker C	Sept. 1974	sediment removal manual burning digging	> 11 yrs
Brittany, France *Amoco Cadiz*[c]	*Salicornia* *Suaeda* *Halimione*	Arabian light Iranian light Crude Bunker C No. 2 fuel	March 1978	sediment removal	5 – > 8 yrs
West Falmouth, Mass. *Florida*[d]	*Spartina alterniflora* *Salicornia europaea* *Spartina patens*	No. 2 fuel	Sept. 1969	?	> 8 yrs
Buzzard's Bay, Mass. *Bouchard 65*[e]	*Spartina alterniflora* *Salicornia virginica*		Oct. 1974	?	> 3 yrs

[a]Baker et al., 1993
[b]Vandermeulen and Jotcham, 1986
[c]Baca et al., 1987
[d]Burns and Teal, 1979; Teal et al., 1992
[e]Hampson and Moul, 1978

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TABLE 5-5 Examples of Oil-impacted Marshes with Recovery Times of 3 Years or Less, Documented by Follow-up Studies (from Hoff et al., 1996)

Location	Vegetation	Oil Type	Time of Oiling	Cleanup	Recovery Time
Hackensack estuary, N.J. Wellen tank farm[a]	*Spartina alterniflora*	No. 6 fuel	May 1976	none cutting	?
Galveston Bay, Tex. Bayou pipeline[b]	*Spartina alterniflora* *Juncus roemerianus*	light crude	Jan. 1984	none sorbents flushing	8 mos – > 2-5 yrs
Harbor Island, Tex. Am Petrofina pipeline[c]	*Spartina alterniflora* *Avicennia germinans*	crude oil	Oct. 1976	none sorbents burning clipping	6 mos – > 6 mos
Aransas River, Chiltipin Creek[d]	*Spartina alterniflora*	S. Texas light crude	Jan. 1992	burning	> 2 yrs
Neches River, Tex. *Esso Bayway*[e]	*Spartina patens*	Arabian crude	Jan. 1979	none sorbents flushing burning cutting	7 mos > 7 mos
Neches River, Tex. Unocal[f]	*Spartina alterniflora*	light crude	April 1993	none sorbents	?
Nairn, La. Shell pipeline[g]	*Spartina patens* *Spartina alterniflora* *Distichlis spicata*	Louisiana crude	April 1985	flushing trampling	< 1-5 yrs

[a]Mattson et al., 1977
[b]Alexander and Webb, 1987
[c]Holt et al., 1978
[d]Tunnell and Hicks, 1994
[e]McCauley and Harrel, 1981; Meyers, 1981; Neff et al., 1981
[f]NOAA, 1993
[g]Mendelssohn et al., 1990; Fischel et al., 1989

out dispersants (Getter et al., 1985), tidal height and range, oil residence time, and season of the oiling. Oiling effects on mangroves differ with life history state and may affect the growth forms of young trees (Getter, 1982; Devlin and Proffitt, 1996). A primary cause of death in oiled mangroves is reported to be the disruption of gas exchange when aerial roots are coated with oil and can no longer supply oxygen to root tissues below ground in hypoxic soils (Teas et al., 1993). Oil can also be taken up by the root system, translocated to leaves, accumulate in the stomata, thereby interrupting transpiration (Getter et al., 1981, 1985). Oil can also disrupt root membranes and allow lethal concentrations of salt to accumulate in mangrove tissues (Page et al., 1985).

Oiling of mangroves following spills can lead to the death of those plants and ultimately unstable habitats and sediment erosion (Nadeau and Berquist, 1977; Duke and Pinzon, 1993; Garrity et al., 1994). Following the death of large numbers of mangrove trees after the Galeta oil spill in Panama, many trees rotted and fell, seagrass rhizome mats disappeared, and sediments from these habitats eroded at rates up to several centimeters per day (Jackson et al., 1989; Keller and Jackson, 1993; Box 5-5). The eroded sediments and oil in various stages of degradation were deposited in neighboring habitats including seagrass beds and coral reefs, which had not been contaminated in the original spill. In many instances the residence times of oil in these deep mud habitats have stretched to decades, which prolongs ecosystem recovery.

The degree of impact to mangroves is a function of the oil type, spill volume, duration of re-oiling, extent of oil coverage on exposed roots, and degree of substrate oiling. Light, refined products can be acutely toxic, for example the jet fuel spill in Puerto Rico that killed 5.5 ha of adult trees (Ballou and Lewis, 1989). Heavier types of oil can lead to eventual death by smothering. Slicks passing though forests at high water often leave a band of oil at the water line, with minimal impacts to the trees. Greatest impacts occur where sediments are contaminated, such as along intertidal berms (Getter et al., 1981). Black mangroves are most sensitive to oil because they osmoregulate by passing materials through the roots and the vascular system, and then out of the leaves

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through specialized glands on the leaf surface. When black mangroves are oiled, this osmoregulatory process facilitates the uptake of oil (Getter et al., 1985). Impacts can be spatially variable (healthy trees adjacent to dead trees) and delayed for years. Because of the potential for damage during cleanup and to the difficulty of access into mangrove forests, intrusive cleanup is considered only under very heavy oiling conditions (e.g., the Galeta spill in Panama).

Recovery of oiled mangroves depends on the initial and residual oil loading as well as damages resulting from cleanup efforts. Physical and chemical weathering of oil may be fairly rapid, occurring over a few months to a year, or gradual and long-term (Burns et al., 2000; Figure 5-6).

Two researchers have attempted to predict the rates of recovery of oiled mangrove habitats; each of these analyses is summarized in Table 5-6. The earliest effort to describe the phases of recovery of oiled mangroves was by Lewis (1981). He proposed the generalized response stages shown in Table 5-6, based on his experience at spills in Florida (T/V *Howard Star*) and Puerto Rico (T/V *Zoe Colocotronis*) and a synthesis of the literature at that time. Lamparelli et al. (1997) conducted a nine-year study of a crude oil spill site along a tidal channel in Brazil with a tidal range of 1-5 m. They measured leaf area and herbivory, tree density, basal area, and tree height for *Rhizophora mangle*, *Laguncularia racemosa*, and *Avicennia schaueriana*.

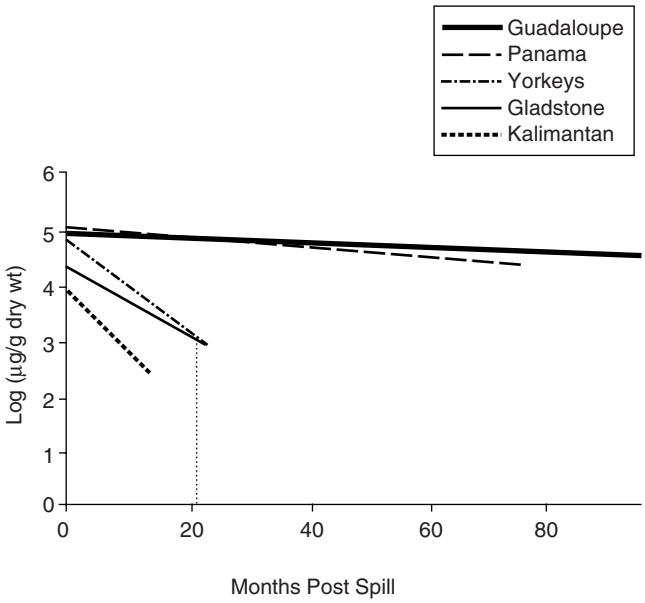

FIGURE 5-6 Loss of oil from Pacific region mangrove sediments. Dotted line indicates time predicted for beginning of recovery of benthic fauna at Gladstone (from Burns et al., 2000, *Marine Pollution Bulletin*).

TABLE 5-6 Proposed Stages of Impact and Recovery of Oiled Mangroves

Author	Stage/Phase	Response
Lewis, 1981	Acute	
	0-15 days	Death of birds, turtles, fish, and invertebrates
	15-30 days	Defoliation and death of small (<1m) mangroves; loss of aerial root community
	Chronic	
	30 days–1 year	Defoliation and death of medium (<3m) mangroves; tissues damage to aerial roots
	1-5 years	Death of larger (>3m) mangroves; loss of oiled aerial roots and regrowth of new ones (sometime deformed); recolonization of oil-damaged areas by new seedlings
	1–10 years?	Reduction in litter fall, reduced reproduction, and reduced survival of seedlings; death or reduced growth of young trees colonizing oiled site? increased insect damage?
	10–50 years?	Complete recovery
Lamparelli et al., 1997	Initial Effect 0-1 year	Seedlings and saplings die; no structural alterations can be measured
	Structural Damage 1-4 years	High mortality is observed, and the oil impact can be measured in terms of major structural alterations
	Stabilization 4-9 years	No or few additional alterations to the structural parameters; sapling growth is observed
	Recovery > 9 years	It is possible to measure improvements in the structural tree parameters; ecosystem may not recover fully to its original state

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Intertidal Shores

Rocky intertidal shores are quite susceptible to damage by oil spills depending on the amount and characteristics of the oil to which they are exposed. The 1985 *Oil in the Sea* report adequately characterized the damage of shorelines to spills and stressed the critical role of geomorphology in the recovery of these shorelines. We reiterate here the importance of the interactions of wave and tidal energy with shoreline geomorphology in determining recovery and punctuate this with lessons from more recent studies.

The persistence of the oil and the time to recovery are a function of the energetic fluxes where oil is deposited. If the initial oiling from a spill is an outer, exposed coast, and the rocky substrate is continuous without substantial low energy interstices, then oil will not persist long and recovery will be relative quick (e.g., see Chan, 1977 for an account of recovery on heavily oiled rocky coasts after the San Francisco Bay spill). If the shoreline is relatively sheltered or there are significant interstices where the oil can enter and be sheltered from the energetic fluxes of waves and tides, then oil will persist and recovery may take substantially longer.

The degree of impact and recovery from a spill on the rocky intertidal is very much a function of the circumstances of a spill. Not only is the aforementioned geological structure of the shoreline important, but the type of oil, the weather conditions following the spill, the thickness and lateral continuity of the slick, the time of year, and the recent history of disturbance of the biological communities are all important factors affecting severity of impact. One example of how low energy environments can retain oil and effects can persist is a southern ocean spill at Macquarie Island. In this spill, most intertidal components appear to have recovered within several years after the spill occurred, but in the holdfasts of kelp, which is an environment not unlike mussel beds, oil was retained for years and the fauna of this microhabitat has not recovered (Smith and Simpson, 1995).

By far the greatest acute injury to intertidal communities as a whole arises from direct contact with oil. Heavy deposits of oil essentially smother intertidal organisms. Toxicity also occurs from elevated concentrations of the soluble components of oil in small pools of water, in wetted surfaces and in the water of rising tides. The common organisms found on rocky intertidal shores of North America—*Fucus*, mussels, periwinkles, starfish, and barnacles—are all susceptible to the toxic effects of oil (Chan, 1977; Stekoll et al., 1993). Recovery of these components can be quite substantial within a year or two, or nearly complete. Subtle long-term effects are possible, however (Peterson, 2001). In the *Exxon Valdez* spill, the aggressive washing of the intertidal rock shores resulted in loss of a significant amount of silt from the rock interstices and the associated bivalve fauna has not been fully re-established and may not be until these sediments have been replenished by natural processes (Driskell et al., 1996).

The above caveats about the nature of the oil, the thickness and extent of the slick and the weather conditions determining impact also apply to softer substrates. Of particular note is the stranding of oil in protected, low-energy environments, such as bays and harbors. If oil arrives in one of these otherwise low-energy environments under storm conditions and gets worked into the substrate, it will likely be there for years and possibly decades. Two examples are the *Florida* spill in West Falmouth, Massachusetts in 1969 (Burns and Teal, 1979) and some areas affected by the *Amoco Cadiz* spill in France in 1978 (Dauvin and Gentil, 1990). It was clear at the time of the *Oil in the Sea* report (NRC, 1985), that the combinations of circumstances resulting in acute effects can also result in recovery times of years and even decades.

In the last 17 years there has been more focus on chronic contamination by PAH, the sensitivity of meiofauna, and indirect effects mediated by changes in predator-prey relationships, as well as by the direct toxic impacts. In particular, chronic exposure of fauna and potential effects have been studied over more realistic time scales and concentrations. Microcosm experiments where realistic doses of PAH are maintained in sediments to provide a chronic exposure regime have been particularly valuable. For example, in salt marsh sediments in Louisiana concentrations of high molecular PAH (up to 16 ppm) were found to decrease the biomass of epibenthic diatoms and cyanobacteria after 4-day exposures, with some indications that snails from high exposure treatments lost weight after initial gains (Bennett et al., 1999). Such experimental results point to the need to examine more closely estuarine food webs where concentrations of PAH in this range can be found.

The spatial scale of the affected sand or mud shoreline area will determine the rebound of the affected area. A practical example of this is the impact of the *Amoco Cadiz* oil spill on benthic crustaceans. Failure to recover in some subtidal habitats was due to the fractionated distribution pattern of favored habitat by some species of amphipods (Dauvin and Gentil, 1990). Nevertheless, the populations were able to recover; densities on the impacted site attained high values similar to those found before the spill within 15 years (Dauvin, 1998).

Subtidal Areas

Oil can arrive in the subtidal by two mechanisms. Surface oil can weather, lose buoyancy and eventually sink, and it can associate with particulate matter suspended in the water and eventually sink, thereby affecting the benthic community (Elmgren et al., 1983). A second route of oil to the benthos is the transport of oil or contaminated particles from nearby oiled beaches.

As with the intertidal fauna, the most sensitive organisms in the subtidal benthos appear to be the crustaceans. Major effects on the crustacean fauna were documented in the

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Tsesis spill (Elmgren et al., 1980), the *Florida* barge spill (Sanders et al., 1980), the *Amoco Cadiz* spill (Dauvin and Gentil, 1990), the *Exxon Valdez* spill (Jewett et al., 1999), and the 1996 *North Cape* oil spill where 8 to 9 million American lobsters were killed subtidally from a fuel oil spill (McCay, 2001). In addition, the rhepoxiniid amphipods, which appear to be particularly susceptible, are one of the few severely depressed faunal components in the benthic communities in areas of moderate petroleum seepage in the Santa Barbara Channel (Davis and Spies, 1980).

Not all spills demonstrated adverse effects in subtidal habitats. A study of the possible effects of tar residues from the *Haven* oil spill in Italy revealed no discernable differences between tar-affected and non-affected benthic communities (Guidetti et al., 2000). *Exxon Valdez* oil was generally not discernable below 40 meters in most portions of Prince William Sound and was never found in measurable quantities below 100 m depth. It is not surprising then that a study of deep benthic communities found no differences between various areas that could be attributed to oil from the spill (Feder and Feder, 1998).

During the *Braer* spill off the Shetland Islands, 84,700 tonnes of a light Gullfaks crude oil were released from the grounded vessel during hurricane-force winds, and an estimated 35 percent of the oil was deposited on the seabed in water depths from 2-100 m in an area of 4,000 km^2 (Kingston, 1999). The sedimented oil provided a long-term pathway for exposure to benthic fisheries. For example, burrowing Norway lobster (*Nephrops*) remained contaminated for over five years, whereas epibenthic lobsters (*Homarus*) eliminated petroleum contaminants to background levels of PAH in one month (Kingston, 1999).

Effects Associated with Various Sources

As discussed in Chapter 3, petroleum enters the marine environment from a variety of sources, at different rates, and in diverse settings. Understanding how the environment responds to releases associated with specific sources is an important aspect of understanding the overall impact of widespread extraction, handling, and use of petroleum hydrocarbons.

Lessons from Natural Seeps

Natural petroleum seeps occur in many parts of the ocean, and can be utilized to understand the effects of oil contamination (Spies et al., 1980). As petroleum enters the ocean from the seabed, it is relatively unweathered in comparison to many other sources of oil that reaches the bottom (Reed and Kaplan, 1977; Steurmer et al., 1982). There are some significant consequences to this difference that limit the usefulness of oil seeps as effects models for other sources of oil in which weathering occurs before the oil is deposited in bottom sediments. Also, the possibility must be kept in mind that, with a history of thousands of years, animals living near seeps might have unique adaptations. Biological studies of seeps have concentrated on the extensively contaminated benthos (Spies and Davis, 1979; Spies et al., 1990).

There are two aspects to the effects of fresh seeping petroleum on benthic ecosystems. First, fresh petroleum, being a highly reduced source of energy, is readily oxidized by microbes (Bauer et al., 1988), which, in turn, can serve as a supplementary food source for benthic food webs in shallow water (Spies and DesMarais, 1983; Bauer et al, 1990). In the case of seeps in deep water, it can be a nearly exclusive carbon source. Second, at sufficiently high concentrations, the aromatic components of seep petroleum are toxic to marine organisms (Davis et al., 1981). There is also an interaction between toxicity of oil and microbial metabolism of petroleum. The decrease in oxygen in the surface layers of the sediments that results from microbial metabolism of petroleum is a limiting factor to benthic organisms. The oil, while supporting microbial growth that acts as a food source, may also be toxic to other organisms or indirectly decrease habitat quality through oxygen deficiency (Spies et al., 1989; Steichen et al., 1996). Microbial transformations of aromatic hydrocarbons may alter hydrocarbon composition and various oxidized products may be formed (Bartha and Atlas, 1987). Natural biogeochemical tracers indicate that both the petroleum carbon, particularly the lighter fractions, and sulfur from sulfide is incorporated into benthic meiofauna and macrofauna (Spies and DesMarais, 1983; Bauer et al., 1990). Circumstantial evidence for damage to gill tissues in bottom-feeding surf perches are linked to oil exposure through cytochrome P450 1A induction and aromatic petroleum metabolites in bile (Spies et al., 1996).

The most detailed investigations of petroleum seepages have been carried out in the Santa Barbara Channel off the coast of southern California. The following summarizes the findings of studies conducted at a depth of 20m in one of these oil seep areas, the Isla Vista seep. Starting with the fresh oil and gas in the sediments of a petroleum seep, several related phenomena occur. Bacterial populations, as measured by ATP content or by direct microscopic counts, are elevated several fold over surrounding sediments (Spies et al., 1980; Bauer et al., 1988). The sediments are highly reducing, oxygen is undetectable in sediments below a very thin surface layer, sulfate oxidizing activity is markedly elevated, hydrogen sulfide is abundant, and sulfide-oxidizing bacteria (*Beggiatoa*) are abundant at the surface of sediments, often forming prominent white mats.

The heavy seepage areas where the *Beggiatoa* mats form support a low-diversity benthic community consisting of large numbers of nematodes, a few polychaete worms (e.g., *Capitella capitata*), some oligochaete worms, and a limited number of harpacticoid copepod species (Spies et al., 1980; Montagna et al., 1987, 1989, 1995). Porewater concentrations of aromatic hydrocarbons within a few centimeters of an active seep were approximately 1 ppm. The nematodes

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form a halo of high abundance, often only a few centimeters from the most active sources of seepage. Within several meters of the very active seeps, and where a small amount of seepage is still found, a diverse benthic community occurs of mainly detrital feeders. This community is similar in composition to the surrounding community that occupies much of the inner continental shelf in southern California. There are some key differences: oligochaetes are a significant component of the community, and some rhepoxiniid amphipods that are particularly sensitive to oil are missing but are found outside the seepage area (Davis and Spies, 1980). Also, in comparison to a nearby station, this community has a consistently larger number of organisms per unit area of sandy bottom.

Based on these findings the following is a conceptual model of the shallow water seep system in the Santa Barbara Channel. The lighter fractions of seeping petroleum are metabolized by microbes, and the energy in the petroleum is partially converted into microbial biomass. Rapid utilization of oxygen by microbial petroleum oxidizers shifts sediment biochemistry to sulfate oxidation and the resulting product, hydrogen sulfide, is utilized by sulfide oxidizers (*Beggiatoa*). At some distance from areas of active seepage, where pore water aromatic hydrocarbon and sulfide concentrations drop to tolerable levels and oxygen can penetrate further into the surface layer of the sediment, the diversity of organisms increases. Bacteria that assimilate and oxidize petroleum are utilized by meio- and macrofauna as an additional source of energy to supplement the usual contemporary photosynthetic sources of carbon for nearshore benthic communities. This pattern within the benthic community is broadly similar to that described for other sources of organic enrichment in the ocean, e.g., sewage and paper mill wastes (Pearson and Rosenberg, 1978).

In very deep water hydrocarbon seeps, most of the carbon utilized by mussels can originate from petroleum, because little surface water primary production is available. Various microbial chemosynthetic endosymbionts may be present in association with macrofauna of deepwater seeps. These microbes can oxidize either hydrogen sulfide or methane. Methane oxidizers then become carbon sources for their hosts. Methane oxidation has been little investigated in shallow water benthic systems, but could be an important process.

Since the shallow water seeps in southern California occupy only a small fraction of the continental shelf and seep benthic communities are composed almost predominantly of species with wide dispersal mechanisms (particularly in the larval stage), the studies of these "open" communities leave unresolved the issue of multi-generational effects of oil exposure.

Production Fields as Tutoring Grounds

Production fields offer an opportunity for uncovering long-term, chronic effects of petroleum hydrocarbons in the marine environment. Production fields are common in U.S. estuaries, primarily in the northwestern Gulf of Mexico, but are also increasing globally. In the United States, offshore oil and gas production has been limited primarily to continental shelf waters but continues to progress into deeper waters seaward of the shelf break. Regulations regarding the use of oil-based drilling fluids differ globally, as do regulations concerning the discharge of produced waters within U.S. state and federal waters and globally, so that practices that would contribute to the long-term accumulation of contaminants differ regionally as well as with time as regulations change. Still, practices that are currently disallowed in many coastal environments may continue to be allowed in other areas, and as oil and gas production expands globally into developing countries permitting regulations may allow practices there that are currently disallowed in U.S. waters. Thus, lessons learned from various practices, even if currently disallowed, provide the tutoring ground for further production globally.

Because of the continued inputs of drilling fluids and produced water discharges into estuarine, coastal and marine receiving waters, production fields are likely to illustrate long-term, low-level, chronic biological effects in sedimentary habitats resulting from the persistence of metals and medium and high molecular weight aromatic hydrocarbons, heterocyclics and their degradation products. Chronic contamination may result from continuous or intermittent discharges (produced waters, drilling fluids, deck washings) or from repetitive, accidental spills (numerous small spills and/or a small number of major spills during the life of a field). The effects of these effluents are complicated by the addition of drilling discharges accumulated during field development (as opposed to exploratory drilling).

Drilling Fluids and Produced Waters

The major discharges associated with exploratory and development drilling are drilling cuttings and drilling fluids. Drill cuttings are particles of crushed sedimentary rock produced by the action of the drill bit as it penetrates the formation. Their accumulation on the ocean floor alters the benthic sedimentary environment. Drilling fluids are mixtures of natural clays and/or polymers, weighting agents and other materials suspended in a water or oil-based material. Oil-based drilling fluids have never been permitted for discharge to U.S. state or federal waters. Discharges of oil-based mud cuttings were permitted to waters of Canada, the North Sea countries, Australia, and several other offshore regions in the world until recently. Their ocean discharge has been banned in most of the world. Several metals of environmental concern found in drilling fluids are arsenic, barium, chromium, cadmium, copper, iron, lead, mercury, nickel, and zinc.

During production of oil or gas from a platform, produced water from the formation may be discharged to the environment. Besides being more saline than sea water, produced

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waters contain elevated concentrations of radionuclides, metals, volatile organic aromatic compounds, monoaromatic hydrocarbons, light alkanes, higher molecular weight aromatic hydrocarbons, ketones, phenols, and organic acids. The environmental effects that may result from oil and gas production in a field depend greatly on the characteristics of the receiving environment. For example, there was a decreased abundance of fouling organisms, particularly barnacles, from the surface to a depth of about 3 m on a platform leg immediately below the produced water discharge located 1 m above the water surface (Howard et al., 1980). Produced water discharges, however, are usually dispersed to some degree. If discharged into the ocean, the produced water dilutes rapidly so that no impacts are ascribed to salinity. In more confined estuarine waters, produced water discharges form dense, saline plumes that move along the bottom sediments, but the resulting elevated water column and interstitial sediment salinity levels are within the range of tolerance of euryhaline estuarine organisms. In shallow, more confined areas with high suspended sediment loads or fine-grained sediments, medium molecular weight hydrocarbons and metals can absorb to particles and be deposited. Measurable effects are most likely in shallow waters, areas of restricted flow and dispersion, water with a high concentration of suspended particulates, and areas of fine-grained anaerobic sediments.

Effects of Production Discharges in Estuarine Waters

U.S. regulations now prohibit most discharges of produced waters from platforms to state waters of Texas and Louisiana, although the phase-out is not yet complete and some exceptions are provided, for example the highly dispersive distributaries of the Mississippi and Atchafalaya Rivers. The discharge of treated produced water from several offshore platforms at shore-based facilities is still permitted in Upper Cook Inlet, Alaska. The discharge of produced waters into estuaries and shallow coastal waters continues globally in developing fields (e.g., Nigeria, Angola, China, Thailand), and the effects of produced water discharges may still linger where the practice has been discontinued (Rabalais et al., 1998).

The effects of produced water discharges in estuaries have been studied extensively in Texas and Louisiana. For example Mackin (1971) surveyed estuarine benthic communities in eight Texas bays receiving produced water effluents. He reported no effects in two bays, minor localized effects in several other bays, and a zone of severely depressed fauna up to 106 m from submarine outfalls in Trinity Bay, Texas and a zone of enhanced faunal abundance and diversity down-current from there. Mackin (1971), however, conducted no chemical analyses. Armstrong et al. (1979) repeated these studies in Trinity Bay to correlate the benthic community effects with the distribution of hydrocarbons in sediments. In shallow waters of 2-3 m, they demonstrated the impacts of high concentrations of hydrocarbons, in this case sediment naphthalene concentrations of 4 to 8 ppm up to 1200 m from the platform, with corresponding severely depressed benthic fauna.

It was not until the mid to late 1980s that more extensive, systematic studies of the effects of produced water discharges in estuarine waters were conducted. While most surface water disposal was terminated on January 1, 2000, except within the distributary channels of Louisiana's major rivers (the Mississippi and Atchafalaya), it is prudent to review the results of these studies for several reasons. First, this disposal method was practiced in coastal Louisiana and Texas and at one time accounted for 2,500,000 bbl/d of discharges into estuarine waters with the potential in some areas for long-term accumulation of contaminants and subsequent reintroduction to the environment (Boesch and Rabalais, 1989b; Rabalais et al., 1991a,b; Rabalais et al., 1998). Second, accidents associated with current disposal methods (pipelines and barges) will have similar results. Third, surface water disposal in estuarine waters still occurs elsewhere in the world.

Boesch and Rabalais (1989a), Neff et al. (1989), St. Pé (1990), Rabalais et al. (1991a,b), Steimle & Associates, Inc. (1991), Mulino et al. (1996) studied the effects of produced water discharges in estuarine waters of Louisiana. Where suitable measurements were made, the eventual fate of the dispersed produced water and the effects on benthic infauna could be explained by the volume of the discharge, the concentration of the various constituents, and the sedimentary regime, physical structure, and hydrology of the receiving environment (Boesch and Rabalais, 1989; Rabalais et al., 1991a). Dilution of water-soluble contaminants was influenced primarily by the volume of the receiving waters, the current velocity, and the potential for resuspension of sediments. Dispersion of sediment-adsorbed contaminants was influenced by the bed shear stress, sedimentation rates, and the grain size distribution of the surface sediments. The dilution potential of the environment was high for erosional environments with high current speeds and low for depositional environments, with intermediate potential for environments with periodic resuspension (storm-related) and deposition. There were no documented effects on the benthic community due to elevated salinities, because the overlying water and sediment interstitial salinities were within the range of the euryhaline organisms found in these habitats. Volatile hydrocarbons in the water column density plume that disperses across the sediment bed varied from nil to as high as 130 mg/L; alkylated PAH in bottom sediments reached concentrations from 2 to 40 ppm with one value of 100 ppm (Rabalais et al., 1991a,b). The potential for accumulation to depth in depositional environments exists (some sediments contained 30 ppm alkylated PAH at 35 cm depth) (Rabalais et al., 1991a). Produced water source contaminants persisted in surface sediments for two years after cessation of the effluent, as did benthic community effects, and persisted for as

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long as nine years in vertical sediment cores (Rabalais et al., 1998).

The effects of produced water discharges in estuarine systems include toxicity to various organisms and, at the community level, the reduction of infaunal abundance and diversity (reviewed by St. Pé, 1990; Rabalais et al., 1991a). The persistent elevation of sediment hydrocarbon and metal concentrations and modification of benthic communities occurred from within a few hundred meters to up to a kilometer from the discharge.

In the Lake Barre field, Louisiana (one out of five such studies), oysters placed in trays adjacent to a produced water discharge suffered mortality as far as 23 m from the outfall and showed decreased growth rates between 23 and 46 m from the outfall (Menzel, 1950; Menzel and Hopkins, 1951, 1953). Similarly deployed oysters near produced water discharges in Pass Fourchon and Bayou Rigaud, Louisiana, resulted in mortality to oysters, reduced growth in others, and bioaccumulation of alkylated PAH and total hydrocarbons 3 to 18 times above background level (Rabalais et al., 1992). The potential for oysters to take up and accumulate contaminants originating in produced water occurred both in close proximity to the discharge and to great distances (350 m at Bayou Rigaud and 1000 m at Pass Fourchon).

Production Effects in Continental Shelf Waters

Several production field studies have been conducted in U.S. offshore waters, in the Norwegian and British sectors of the North Sea field, and on the Dutch continental shelf. [Continental shelf is defined from subtidal barrier shoreface to shelfbreak, usually 200 m water depth.] Because continental shelf ecosystems are complex, open and dynamic, there are fundamental problems in identifying the nature and extent of environmental effects and in determining causality. Any studies conducted in production fields must be designed and interpreted within the context of natural variability and other environmental factors that are important in shaping the physical environment and biological communities. In addition, there is a range of biological, chemical and statistical techniques that can be applied to any of these studies, often suitably, but just as often not. The complicating factors of natural variability have plagued many studies of oil and gas production effects in the northern Gulf of Mexico where one would be most likely to expect to find demonstrable effects on marine ecosystems. Two studies—the Offshore Ecology Investigation (OEI) and the Central Gulf Platform Study—were conducted in coastal Louisiana where extensive oil production activity might make this area a worse case scenario for effects. The locations just west of the Mississippi River delta, however, confounded possible oil-related effects with ecological factors of salinity variability, turbidity, high organic loading, sediment type, and seasonal bottom-water hypoxia (low dissolved oxygen concentrations).

Following 25 years of oil production in both Timbalier Bay and the area directly offshore on the continental shelf in 5 to 25 m water depth, the OEI study (reviewed by Neff, 1987; Spies, 1987) was designed to examine both localized platform effects, and the overall "health" of the ecosystems in the study area. The conclusions of the study (Menzies et al., 1979) were that there were no effects and that (1) natural phenomena in the area were a greater impact than petroleum-related activities, (2) petroleum contamination in the area was low and could not be tied to platform sources, and (3) the region was in "good ecological health." The OEI study was criticized by Sanders (1981) who pointed out faults in study design, laboratory procedures, insufficient contaminant data, and inappropriate statistical treatment of benthic data. A second group of scientists independent of the OEI effort concluded that chemical contaminant data were insufficient to draw conclusions and that the benthic data indicated that the communities were more likely controlled by estuarine- and riverine-influenced salinity and turbidity than by adverse effects of oil (Bender et al., 1979).

The Central Gulf Platform study (water depths of 9 to 98 m; reviewed by Neff, 1987 and Spies, 1987) corrected many of the shortfalls of the OEI study by employing a larger variety of analyses, but was again situated in an area influenced by the Mississippi River, with confounding effects of turbidity, fluctuating salinity, seasonal hypoxia, and potential additional anthropogenic inputs of petroleum (Bedinger et al., 1981). In addition, a major tropical storm likely affected the benthic communities mid-way through sampling. Meiofaunal and macrofaunal benthic data analyzed with clustering techniques identified groups of fauna that were most similar with regard to depth, salinity, distance from shore (= sedimentary characteristics) and dissolved oxygen. Chemical analyses revealed both low and high molecular weight hydrocarbons often in very high concentrations, but there were no consistent patterns with regard to the amount of production from the platform, the age of the platform, or distance from the platform. Conclusions that the Mississippi River was the probable principal source of hydrocarbons to the study area were not supported by the data. The implications in the study conclusions that hydrocarbons were having a chronic sublethal effect on the fauna of the study area were criticized by Spies (1987), because of extrapolation of laboratory toxicity literature to concentrations of hydrocarbons found in the field. That is, most of the toxic effects documented in the literature were from relatively low molecular weight aromatic hydrocarbons, and the sediment hydrocarbons in the Central Gulf Platform study were dominated by highly-weathered mixtures.

Rabalais et al. (1993) tested specifically for the differences in hypoxia versus effects of petroleum production at two production platforms in 20 m water depth. Hydrocarbon concentrations, in general, were low for both study sites (even where sediments were silty) and were characterized as weathered petrogenic or biogenic in nature. There were no

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consistent patterns of benthic community structure with distance from either discharge nor were there any relationships with petroleum indicators. As found in other studies, dissolved oxygen concentration, bottom water temperature and salinity, and sediments were the important environmental factors that explained the variation in benthic community parameters of species richness and abundance.

In a shallower area of the continental shelf (2 m) just offshore of the lower end of Atchafalaya Bay where uniformly silty sediments dominated and the environment was expected to be dispersive, a clear signal of produced water-associated contaminants and effects on benthic biota were observed to at least 200 m and 300 m, respectively (Rabalais et al., 1991a). The shallow water column at this site and flushing potential of Atchafalaya River discharge were expected to dilute and transport the produced water effluents away from the area. The high silt content of the sediments, the large volume of produced water discharged (21,000 bbl/d), and the high concentrations of volatile hydrocarbons may have been factors in the pronounced produced-water-effect at this station. By contrast, a nearby station in 8-m water depth, where the discharge of produced water was an order of magnitude less, was contaminated only within 20 m of the discharge where benthic fauna were also impacted (Neff et al., 1989).

Several production platforms in southern California were assessed for oil and metal contamination and affected marine communities (18 to 30 m water depth; reviewed by Neff, 1987). There were some elevated levels of production contaminants in sediments directly under and adjacent to platforms, but no concentrations of metals and petroleum hydrocarbons in selected fish and mussels. The platforms, piles of cuttings, and biofouling organisms both on the platforms and those sloughed to the bottom functioned as artificial reefs, providing habitats for a wider variety of marine animals than occurred on nearby hard and soft bottoms. In a study of a produced water discharge outfall in a high energy subtidal (10-12 m) environment off southern California, Osenberg et al. (1992) indicated that benthic infaunal community effects were localized within 100 m of the outfall.

In offshore waters around production platforms in the Gulf of Mexico, there was little evidence of bioaccumulation of produced water contaminants in edible tissues of resident fishes and invertebrates (Continental Shelf Associates, Inc., 1997). For the southern California produced water outfall in a high energy subtidal zone, Osenberg et al. (1992) found that the effects on outplanted mussels were more widespread than on the benthic infauna, between 500 and 1000 m from the outfall, as opposed to within 100 m. The observed effects on the mussels were reduction in growth, condition, and tissue production and varied inversely with relative exposure of the mussels to the produced water plume.

Two major studies have been conducted on the Texas continental shelf to examine the ecological effects of chronic contamination as well as sublethal impacts. These studies were conducted away from the influence of the Mississippi River and focused on near-field effects with a closer link between biological and chemical analyses. The Buccaneer Gas and Oil Field study (20 m depth; Middleditch, 1981) documented persistent accumulation of sediment hydrocarbons only within about 100 m of the platforms, but did not provide a thorough analysis of the chemical constituents present. A widespread effect on the benthos, including reduced numbers of individuals and species around the platforms, was apparent, but there were also areas well away from the platforms with similar benthic communities.

The Gulf of Mexico Offshore Operations Monitoring Experiment (GOOMEX) was designed to test and evaluate a range of biological, biochemical and chemical methodologies to detect and assess chronic sublethal biological impacts in the vicinity of long-duration activities associated with hydrocarbon production (Kennicutt et al., 1996b). The study was located in a gas field in the western Gulf of Mexico continental shelf and as removed as possible from confounding effects of Mississippi River discharge. The three platforms were in progressively deeper water, 29, 80 and 125 m. Sediments close (< 100 m) to the three platforms studied were enhanced in coarse-grain materials primarily derived from discharged muds and cuttings. Hydrocarbon and trace metal (Ag, Ba, Cd, Hg, Pb, and Zn) contaminants were associated with these coarse-grain sediments (Kennicutt et al., 1996a). Contaminants were asymmetrically distributed around each platform in response to the prevailing currents. The positive relationship between sand content and contaminant levels is contrary to the view of contaminants being associated with finer-grain sediments (Peterson et al., 1996).

The hydrocarbons occurred in concentrations that seemed too low to be important contributors to the observed toxicological effects. PAH were generally less than 100 ng/g, which was an order of magnitude lower than what Spies (1987) suggested was needed to induce biological response. At a few locations close to one platform, trace metal (i.e., Cd, Hg, Pb, and Zn) concentrations exceeded levels thought to induce biological effects. In deeper water (> 80 m), sediment trace metal contaminant patterns were stable over time frames of years. A few metals (Pb, Cd) exhibited evidence of continued accumulation in sediments over the history of the platform at the deeper water sites (> 80 m) immediately after cessation of drilling cf. 5-10 years after the last discharges. The chemical contaminants principally originated from the original drilling mud discharge and perhaps from produced waters during production (Kennicutt et al., 1996b).

Sediment chemical analyses and porewater toxicity tests with sea urchin fertilization and embryological development assays from the GOOMEX study (Carr et al., 1996) indicated toxicity near four of the five platforms, the majority collected within 150 m of a platform and those with the highest concentrations of contaminants. There was agreement among results of porewater tests with three species (sea urchin embryological development, polychaete reproduction,

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and harpacticoid nauplii survival). Samples from the deepest site (> 80 m, HI-A389 near the Flower Gardens), which contained the highest contaminant concentrations, were the most toxic samples of the sites. Repeatability of toxicity between seasons demonstrated the persistence of the toxicity.

The meiofauna and macrofauna effects (Montagna and Harper, 1996) were localized within 100-200 m from the platforms (Table 5-7). The patterns of community change were increases in deposit-feeding polychaetes and nematodes that indicated organic enrichment, while density declines of harpacticoid copepods and amphipods indicated toxicity. The increase in annelids closer to the platforms occurred despite the steep gradient in sand content; total annelids would be expected to be more abundant in finer sediments, not coarser. In contrast with annelids and oligochaetes, amphipod abundances were depressed around all platforms, with effects confined to 50 to 100 m. This was also consistent with literature on modest pollution, and is suggestive of a toxic response. Sea stars were reduced near the platform, but that pattern did not hold for ophiuroids. Changes in meiofaunal responses were most noticeable within 50 m of platforms. Harpacticoid abundance, community diversity, genetic diversity, reproductive success and survivability declined nearer the platforms with an increasing contaminant gradient at all study sites. On the other hand, total nematodes were enhanced. Patterns were absent at the shallowest site (29 m, MAI-686) where the relatively high-energy physical environment has led to more extensive dispersion of materials discharged. The other sites were in 80 m (MU-A85) and 125 m (HI-A389). They concluded that patterns of response to sedimentary contamination were detectable at higher taxonomic levels, and that these responses were driven by intrinsic physiological and ecological characteristics of higher taxa. Crustaceans (especially amphipods and harpacticoid copepods) and echinoderms are sensitive to toxics whereas polychaetes, oligochaetes, and nematodes (especially nonselective deposit feeders) are enhanced by organic enrichment (either from hydrocarbons or biologically produced materials falling from the platform structure). They concluded that metals drove the toxicity effects, and that the dual effects of toxicity and organic enrichment resulted in readily detectable responses in benthic meiofauna and macrofauna to 100-200 m.

TABLE 5-7 Responses of Biological and Ecological Indicators to Distance from Platforms in the Gulf of Mexico (compiled by P. Montagna)

	Platform		
Indicator	MAI-686 29 m depth	MU-A85 80 m depth	HI-A389 125 m depth
Macroinfauna			
Total Abundance	0	↑70 percent	↑3-5×
Polychaete (P) Abundance	0	↑90 percent	↑3-5×
Amphipod (A) Abundance	↓4-12×	↓4-5×	↓3-5×
P:A ratio	↑6-10×	↑8-10×	↑20-30×
Meiofauna			
Total Abundance	↓2-3×	0	↑50 percent
Nematode (N) Abundance	↓2×	↓2×	↑60-80 percent
Harpacticoid (H) Abundance	↓2×	0	↓3×
N:H ratio	0	0	↑4-5×
Nematode Production	↓49×	↓135×	↓2-3×
H. Gravid Females	↑3×	0	↑3×
H. Clutch Size	0	↓10 percent	↓14 percent
H. Genetic Diversity	↓2×	↓1-5×	↓2-3×
Megafauna			
Catch Per Unit Effort	0	0	↑
Size	0	↓	↑
Histopathology	0	↑	0
Sex Ratio	0	0	↑Female
Toxicity & Biomarkers			
Pore Water Toxicity	↑	0	↑
Invertebrate AHH	0	0	0
Fish: EROD, PAH in Bile, P4501A mRNA	0	0	0

Summary of results for macrofauna and meiofauna (Montagna and Harper, 1996), nematode production (Montagna and Li, 1997), genetic diversity (Street and Montagna, 1996), harpacticoids reproduction (Montagna, unpublished data), megafauna (Ellis et al., 1996), toxicity (Carr et al., 1996) and biomarkers (McDonald et al., 1996). Table symbols represent percent increase (↑), no change (0), or decrease (↓) from near-field (< 100 m) to far-field stations (100 m to 3 km). 1x = 100 percent.

The GOOMEX studies also focused on chronic, sublethal effects. Various physiological (McDonald et al., 1996) and genetic results (Montagna and Harper, 1996) provided evidence that crustaceans around the platforms were exhibiting sublethal responses to contaminant exposure. The percentage of gravid female harpacticoid copepods was greater and the percentage of juveniles was reduced within 50m of the platforms. In addition, reproductive effort for female harpacticoids carrying eggs was reduced. These responses could be explained as sublethal physiological reactions of these organisms to stress related to exposure to toxicants. The demonstration in multiple species of harpacticoids that genetic diversity was significantly reduced near the platforms and associated with increased contaminants as compared with the far-field sites suggested detection of a sublethal response of these sensitive organisms to some aspect of the platform-associated environment.

Several studies have been conducted in the North Sea (reviewed by Neff, 1987; Spies, 1987). The Ekofisk Oilfield study (70 m water depth) was designed to assess the impacts of ballast water discharge from a one-million barrel oil storage tank placed on the sea bottom, as well as impacts from production platforms. The Ekofisk study was complicated by a well blowout, and it is not known whether drilling employed oil-based fluids. Results indicated elevated concen-

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trations of oil constituents around some platforms at Ekofisk. Some faunal change around the platforms could be related to elevated hydrocarbon content, but were more readily explained by the changed sedimentary conditions and associated total organic carbon content surrounding the platforms (Spies, 1987). The Forties Oilfield, developed using only water-based drilling muds, is situated in 100 to 125 m water depth and represents deeper conditions than most studies on the Louisiana and Texas continental shelves. Impacts of oil production activities there were localized, primarily within 450 m of the platforms, and were of low magnitude. Only water-based drilling fluids were used in the Buchan field, and no produced water was discharged. No biological impacts of the platform or production activities were detected.

Oil-based drilling fluids were used extensively in the North Sea, and the amounts of petroleum hydrocarbons discharged with drill cuttings and their subsequent accumulation have been documented by several authors, (reviewed by Davies et al., 1983; summarized by Neff, 1987). There are four zones of chemical and biological impact around platforms discharging contaminated cuttings. Zone I, extending out to 250 m and exceptionally to 500 m from the platform, is characterized by hydrocarbon concentrations 1000 times above background and severely impoverished and modified benthos. Zone II extends from 200 to 2000 m from the platform with sediment concentrations 10-700 times above background, modified species diversity, and increased abundance of opportunistic polychaetes. Zones III and IV have normal benthic communities and decreasing gradients of hydrocarbon contamination. At the time of the Davies et al. (1983) review, none of the areas had been studied long enough to determine benthic recovery.

In contrast to the implication of metals over the long-term being the agent of benthic effects in a production field offshore Texas, U.S., the implicated contaminants where oil-based drilling fluids were used over many decades in oil and gas production in the North Sea are the hydrocarbons in those drilling fluids (Grant and Briggs, 2002). In toxicity studies of sediments from around the North West Hutton platform in the North Sea, sediments from 600 m from the platform remained acutely toxic to the amphipod *Corophium* and acutely toxic to the same organism at 100 m from the platform when 3% contaminated sediment was mixed with clean sediment. Metals toxicity was only a factor immediately adjacent to the platform.

Production Fields

There are clear effects of produced water discharges on waters, sediments, and living resources in estuarine production fields where the receiving environment is not conducive to the dispersion of the effluent plume. In shallow shelf waters, hydrocarbons from produced water accumulate in bottom sediments and benthic fauna may be depressed up to 300 m from the outfall. Measurable effects occur around offshore platforms, but except for artificial reef effects, sedimentary changes or changes brought about by a cuttings pile, such effects are usually localized. Beyond some contamination of organisms by petroleum, there is little convincing evidence of significant effects from petroleum around offshore platforms in deeper water. Where oil-based drill cuttings are discharged, there are readily evident effects of sediment contamination and benthic impacts to much greater distances from the platforms (up to 1 to 2 km).

While directed studies have identified some specific sublethal effects of long-term oil and gas development, the most significant unanswered questions remain those regarding the effects on ecosystems of chronic long-term, low-level exposures resulting from discharges and spills caused by development activities. Ultimately, we must determine whether the potential for effects from production fields are significant with regard to the geographic scale, what the cumulative effects are, whether ecosystem integrity is compromised, and whether there are significant impacts to resources that humans value, such as fisheries, marine mammals, endangered species, or rare or aesthetically pleasing environments.

Deep Sea Communities

Unfortunately, our knowledge base for the effects of chemicals or habitat perturbation is the most meager for the deep sea. It is unexpected, however, that ecological processes in the deep sea are fundamentally different from those of the continental shelf. There are additional environmental and physical parameters at work in the deep sea that make populations and communities there unique. What is not known are the sensitivities to contaminants; rates and mechanisms for population control, biological interactions, and recruitment; or rates or potential for recovery from impact.

Unique features of the deep sea and the fauna make them more susceptible to certain types of chemical spills. Increased turbidity from a spilled chemical such as a drilling mud could impact animals adapted to low light (including possibly, those with bioluminescent capabilities) by increased turbidity from deep plumes of low transmission water and indirectly through biological light interactions. Spills of chemicals with labile carbon may alter the local balance of oxygen consumption and result in hypoxia or anoxia, especially in oxygen minimum zones. Microhabitat diversity is a key to deep-sea diversity, and any chemical spill that alters deep habitats will likely have an impact. Chemical spills that disrupt the accessibility of fluxed detrital material for the dominant deposit-feeding organisms will affect feeding and subsequently the health of the organism(s). Chemicals that affect mortality, population levels, biological interactions, recruitment, growth rates, through either acute or chronic, sublethal toxicity or habitat alteration or both are likely to affect soft-bottom benthos in the deep sea similarly to continental shelf organisms. Basic biological information for most deep-sea organisms (e.g., feeding type, reproduc-

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tion, life span, growth rates, predators, and community ecology), however, is nonexistent.

Chemosynthetic seep communities are considered prevalent between 300 and 1000 m water depth on the northern Gulf of Mexico slope. Commonality, however, is not a reason for relaxing criteria for acceptable impact without knowledge of the ability of undamaged or damaged fauna to ultimately repopulate any impacted areas. Some organisms that inhabit the cold seep communities may be extremely old, and damaged communities would be slow or unlikely to recover. Hard bottom communities with highly diverse biogenically-structured communities are afforded protection from drilling operations in the Gulf of Mexico, and any chemical spills that approximate these types of effects would be expected to produce similar harm to live-bottom communities.

Summary

Since the compilation of the 1985 NRC report, *Oil in the Sea*, great progress has been made in identifying the toxic effects of petroleum hydrocarbons in a wide variety of organisms. We have also gained considerable knowledge of the effects of oil on various marine habitats through laboratory experiments, mesocosm experiments and practical experience with spills. Our knowledge of the effects of produced waters has expanded for inshore and offshore production fields and for multiple mixtures of oil and other contaminants in confined water bodies such as harbors. We now have first-hand experience with spills in coral reefs, mangroves, seagrass beds, and high-latitude cold-water environments. We are now in a better position to assess risks to individual organisms and habitats from the production, transport and consumption of petroleum than we were in 1985.

Assessing the effects of any particular spill and recovery from its effects has proven more complicated than was anticipated in 1985. We know that the natural variability of marine ecosystems and the open nature of marine communities, in which recruitment of young may be dependent on planktonic larvae transported from great distances, creates a substantial challenge in assessing both the effects of a spill and recovery from those effects. Although we now know much more about the toxicity and sublethal effects of petroleum hydrocarbons to organisms, we still have great difficulty in assessing the population, community, or ecosystem effects of pollution events. To assess the effects of oil in the sea and recovery from impacts, we need new information on the population structure of these marine organisms that is critical for the function of their communities. In addition, appreciation of the influence of decadal-scale and longer climate change means that we cannot expect communities or ecosystems to return to the state in which they were at the time of a pollution incident. Given the various time-scales of ecosystem change, before-after and control-impacted (BACI) designs for assessing damage are valuable, but they are no substitute for an up-to-date time series from a well-designed monitoring program. Based on an improved understanding of change in the marine environment, there is great value in having time series for detecting change and for pointing to processes critical for understanding change.

The effects of oil in the sea depend greatly on the season, place, and the types of organisms present. Although for a given habitat at a given time, a large amount of oil is likely to create more damage than a small amount, small amounts in sensitive environments or where there are populations at risk can have devastating effects.

Reducing the Threat to the Marine Environment

Ecosystems and their components vary at time-scales from seasons to decades and longer. Therefore, in the absence of on-going monitoring it is exceedingly difficult to quantify the effects of oil in the sea, or to establish when recovery from a pollution event is complete. Establishment of monitoring programs in selected regions with an elevated risk of petroleum spills or discharges would enhance the ability to determine effects and recovery, and to understand the processes controlling ecosystem responses to pollution. Existing databases on the distribution, frequency and size of petroleum spills and existing petroleum and distribution routes could be used to identify locations most appropriate for monitoring. **Federal agencies, especially the USGS and EPA, should work with state and local authorities to establish or expand efforts to monitor vulnerable components of ecosystems likely to be exposed to petroleum releases.**

There are demonstrable effects of acute oiling events at both small and large spatial-scales. These effects result from physical fouling of organisms and physiological responses to the toxic components of oil. Although there is now considerable information on the toxicological effects of individual components of oil, there is a lack of information about the synergistic interactions within organisms between hydrocarbons and other classes of pollutants. This problem is particularly acute in areas subject to chronic pollution, e.g., urban runoff. Research on the cumulative effects of multiple types of hydrocarbons in combination with other types of pollutants is needed to assess toxicity and organism response under conditions experienced by organisms in polluted coastal zones. **Federal agencies, especially the USGS, NOAA, and EPA, should work with industry to develop or expand research efforts to understand the cumulative effects of multiple types of hydrocarbons in combination with other types of pollutants on marine organisms. Furthermore, such research efforts should also address the fates and effects of those fractions that are known or suspected to be toxic in geographic regions where their rate of input is high.**

There are demonstrable sublethal physiological effects of long-term, chronic releases of hydrocarbons into the marine environment. These have been found in areas affected by

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urban runoff, in areas where oil has been incorporated in sediments and is then released back to the water column, and in production fields. Chronic sources of hydrocarbon pollution remain a concern, and their effects on populations and ecosystems need further assessment. **Federal agencies, especially the USGS, EPA, and NOAA should work with state and local authorities and industry to implement a comprehensive laboratory and field based investigation of the impact of chronic releases of petroleum hydrocarbons.**

Biogenically-structured habitats, such as salt marshes and mangrove forests, are subject to destruction or alteration by acute oiling events. Because the structure of these habitats depends upon living organisms, when these are killed, the structure of the habitat, and sometimes the substrate on which it grows, is lost. Depending upon the severity of oiling and particularly if oil is incorporated in the sediments or structure of the habitat, recovery of the habitat and the organisms dependent on it may be exceptionally slow. **In areas of sensitive environments or at-risk organisms, federal, state, and local entities responsible for contingency plans should develop mechanisms for higher level of prevention, such as avoidance, improved vessel tracking systems, escort tugs, and technology for tanker safety.**

Although there is now good evidence for the toxic effects of oil pollution on individual organisms and on the species composition of communities, there is little information on the effects of either acute or chronic oil pollution on populations or on the function of communities or ecosystems. The lack of understanding of population-level effects lies partly in the fact that the structure of populations of most marine organisms is poorly known because of the open nature of communities and the flow of recruits between regions. Also, in some populations, (e.g., bony fish), the relationships between numbers of juveniles produced and recruitment to the spawning adult population are unknown. **The U.S. Departments of Interior and Commerce should identify an agency, or combination of agencies, to develop priorities for continued research on:**

- **the structure of populations of marine organisms and the spatial extent of the regions from which recruitment occurs,**
- **the potential for cascades of effects when local populations of organisms that are key in structuring a community are removed by oiling, and**
- **the basic population biology of marine organisms may lead to breakthroughs in understanding the relationship between sublethal effects, individual mortality, and population consequences.**

There is a tremendous need for timely dissemination of information across state, federal, and international boundaries about the environmental effects of oil in the sea. Although the United States has experience that might benefit the international community, the United States might benefit greatly from lessons learned in other countries with offshore oil production, heavy transportation usage, and diffuse inputs of petroleum from land- and air-based sources. **Therefore, the federal agencies identified above, in collaboration with similar international institutions, should develop mechanisms to facilitate the transfer of information and experience.**

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Appendixes

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A

Committee and Staff Biographies

COMMITTEE CHAIR:

James Coleman
Louisiana State University
James Coleman, received his Ph.D. in geology from Louisiana State University in 1966. He was the executive vice chancellor of Louisiana State University (LSU) from 1989-1998 and presently serves as Boyd Professor in the Coastal Studies Institute of LSU. Dr. Coleman is the former chair of the Marine Board, chair of Minerals Management Service Scientific Advisory Committee, member of the OSB, the NAE and the Russian Academy of Natural Sciences. He presently serves on the President's Ocean Policy Commission. He specializes in coastal and marine geology and his research interests include deltaic sedimentation, riverine processes, and continental shelf sediments.

COMMITTEE MEMBERS:

Joel Baker
University of Maryland
Joel Baker received his Ph.D. in civil engineering with an emphasis in environmental engineering sciences from the University of Minnesota in 1988. He is currently a professor at the University of Maryland's Chesapeake Biological Laboratory. Dr. Baker's expertise includes modeling contaminant transport and fate in natural waters, atmospheric chemistry and the deposition of semivolatile organic contaminants, and modeling accumulation of persistent chemicals in aquatic food webs.

Cortis Cooper
ChevronTexaco
Cortis Cooper received his Ph.D. in 1987 from the University of Maine. He is presently a senior research scientist with Exploration Petroleum Technology Co. (the upstream R&D organization for ChevronTexaco). He is an internal company consultant for oceanographic, meteorological, and oil spill response issues. He has provided technical leadership on a number of large studies including investigations of hurricane alleys, forecasts of Loop Current intrusions, hurricane current modeling, and remote sensing of major storm systems.

Merv Fingas
Environment Canada
Merv Fingas received his Doctorate in environmental sciences from McGill University in Canada in 1996. Dr. Fingas has been with Environment Canada since 1974 and is currently the chief of the Emergencies Sciences Division. He was the chairman of the NATO-CCMS Committee on Spill Studies, analytical section from 1987-1991. Dr. Fingas is a scientist working in spill research and development and specializes in spill dynamics and behavior, spill treating agents, and *in-situ* burning.

George Hunt
University of California, Irvine
George Hunt received his Ph.D. in biology from Harvard in 1971. He is presently a professor of Ocean Ecology at the University of California, Irvine and has published extensively on the foraging ecology of marine birds, mechanisms for trophic transfer to top predators in marine ecosystems and the impacts of oil spills on marine birds. Dr. Hunt is a Fellow of the American Association for the Advancement of Science and the American Ornithologists Union, and has previously served on the National Research Council's Committee on Mono Basin, (1985-1987), the Ecology Subcommittee to review Outer Continental Shelf Environmental Studies Program (1986-1992), and the Committee to review Alaskan Outer Continental Shelf Environmental Information (1991-1994).

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Keith Kvenvolden
U.S. Geological Survey
Keith Kvenvolden earned his Ph.D. in geology from Stanford University in 1961 and he has been with the U.S. Geological Survey since 1975 and a senior scientist since 1992. Specializing in organic geochemistry, Dr. Kvenvolden studies natural and man-introduced hydrocarbons in the marine environment, including crude oil, hydrocarbon gases and gas hydrates.

Judith McDowell
Woods Hole Oceanographic Institution
Judith McDowell received her Ph.D. in Zoology from the University of New Hampshire in 1974. She is currently a senior scientist at the Woods Hole Oceanographic Institution where her research addresses the physiological effects of pollutants on marine benthic communities. Dr. McDowell has been a member of the Ocean Studies Board and the Commission on Geosciences, Environment and Resources and has served on numerous committees for the National Research Council. Dr. McDowell also chaired the panel responsible for the 1992 NRC report Assessment of The U.S. Outer Continental Shelf Environmental Studies Program: Part II-Ecology.

Jacqueline Michel
Research Planning, Inc.
Jacqueline Michel received her Ph.D. from the University of South Carolina in geochemistry in 1980. She is currently with Research Planning, Inc. Dr. Michel is an expert in oil and chemical spill response and contingency planning. She has been the program manager providing scientific support to NOAA's Hazardous Materials Response and Assessment Division since 1978. She is currently a member of the OSB and the Science Advisory Panel to the President's Ocean Policy Commission. Dr. Michel has served on several NRC committees including the Spills of Nonfloating Oils and Spills of Emulsified Fuels.

Keith Michel
Herbert Engineering
Keith Michel obtained his B.S. in Naval Architecture and Marine Engineering from the Webb Institute of Naval Architecture. He has worked at Herbert Engineering Corporation since 1973 and is currently the president. Mr. Michel has experience with risk analysis of maritime activities involving petroleum hydrocarbons, is currently a member of the Marine Board, and has served on several NRC committees including the Committee on Marine Transportation of Heavy Oil.

Jonathan Phinney
American Society of Limnology and Oceanography
Jonathan Phinney received his Ph.D. in biological oceanography from the University of California, Santa Cruz in 1995. He is the Executive Director of the American Society of Limnology and Oceanography after having been with the Center for Marine Conservation (now The Ocean Conservancy) as the water quality scientist and technical advisor. Dr. Phinney's research interests include biogeochemistry and in particular the effects of land-based sources of pollutants on coastal ecosystems.

Robert Pond (until October 1, 2000)
United States Coast Guard
Robert Pond received his Masters in Environmental Policy in 1991 from George Washington University. He spent twenty years in the U.S. Coast Guard traveling extensively, concentrating in marine safety and environmental protection, including oil spill contingency planning. He has worked closely with Mobil Oil, the American Petroleum Institute, and the National Oceanic and Atmospheric Administration. Mr. Pond also spent 4 years as an environmental consultant to government and industry for oil transportation related issues. He is currently working as an Environmental Specialist with the U.S. Coast Guard's Office of Response in Washington, D.C.

Nancy Rabalais
Louisiana Universities Marine Consortium
Dr. Nancy Rabalais received her Ph.D. in zoology from the University of Texas at Austin in 1983. She is currently a Professor at the Louisiana Universities Marine Consortium. Her research interests include hypoxia, eutrophication, estuarine and benthic ecology, and continental shelf ecosystems. Dr. Rabalais is an AAAS Fellow, an Aldo Leopold Leadership Fellow, and a Past President of the Estuarine Research Federation. She has served on Committee to Review the USGS Coastal and Marine Geology Program, and is currently Chair of the Ocean Studies Board and a delegate for the U.S. National Scientific Committee on Oceanic Research.

Larry Roesner
Colorado State University
Larry Roesner received his Ph.D. from the University of Washington in sanitary engineering in 1969. He has more than twenty years experience in water resources, water quality engineering and management. He served as the chief technical officer for Camp Dresser & McKee Inc. (CDM), and national technical director of CDM's stormwater practice. Dr. Roesner is currently at Colorado State University and continues his association with CDM.

Robert B. Spies
Applied Marine Sciences and Biomark
Dr. Robert B. Spies received his Ph.D. from the University of Southern California, Los Angeles in 1971. His research addresses the fate and effects of contaminants, especially of petroleum, in the aquatic environment with an emphasis on coastal fish and benthic invertebrate communities. He is cur-

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rently the president of Applied Marine Sciences and Biomark. Dr. Spies serves as the chief scientist for the *Exxon Valdez* Oil Spill Trustee Council. He is also an editor of *Marine Environmental Research*. Dr. Spies has participated in several NRC functions including the Workshop on Coastal Science and Policy Interactions and the Committee on Exploitation of the Outer Continental Shelf, and contributed the section on oil seeps in the 1985 version of Oil in the Sea.

STAFF:

Dan Walker, (Study Director)
National Academy of Sciences
Dan Walker is a senior program officer at the Ocean Studies Board where he has been since July 1995. Since 1999, Dr. Walker has held a joint appointment as a Guest Investigator at the Marine Policy Center of the Woods Hole Oceanographic Institution. He received his Ph.D. in Geology from the University of Tennessee in 1990. Dr. Walker has directed a number of NRC studies including *Clean Coastal Waters: Understanding and Reducing the Effects of Nutrient Pollution (2000)*, *Science for Decisionmaking: Coastal and Marine Geology at the U.S. Geological Survey (1999)*, *Global Ocean Sciences: Toward an Integrated Approach (1998)*, and *The Global Ocean Observing System: Users, Benefits, and Priorities (1997)*. A former member of both the Kentucky and North Carolina State geologic surveys, Dr. Walker's interests focus on the value of environmental information for policymaking at local, state, and national levels.

Jennifer Merrill
National Academy of Sciences
Jennifer Merrill has been a program officer at the Ocean Studies Board since March 2001. She received her Ph.D. in Marine and Estuarine Environmental Science from the University of Maryland Center for Environmental Science, Horn Point Laboratory. With grants from NOAA's National Estuarine Research Reserve and the Hudson River Foundation, she examined the role of upper estuarine marshes in the nutrient budgets of coastal ecosystems. As a NOAA Knauss Marine Policy Fellow in the office of Senator Carl Levin, she helped to represent the Great Lakes region through the Great Lakes Task Force, a bipartisan, bicameral regional coalition dedicated to protecting the Great Lakes ecosystem through legislative and appropriations action. At the University of Maryland College Park she co-taught a course in Marine Biology and worked as a project manager at the Maryland Sea Grant office.

John Dandelski
National Academy of Sciences
John Dandelski recently joined the Ocean Studies Board staff as a research associate. Most recently, John worked at NAP as a Web and Database Developer. John received his M.A. in Marine Affairs and Policy from the Rosenstiel School of Marine and Atmospheric Sciences, University of Miami in December 2001. His research focused on commercial fisheries' impacts to the benthic communities of Biscayne National Park. John served as the University of Miami Assistant Diving Safety Officer and has worked for the International Oceanographic Foundation, the Center for Marine Conservation, and the Congressional Research Service. John also holds an M.S. in Industrial/Organizational Psychology.

Julie Pulley, Project Assistant
National Academy of Sciences
Julie Pulley has been a project assistant at the Ocean Studies Board since March 2001. She received her B.S. in Biology from Howard University, Washington, D.C. in 1999.

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B

Definitions and Conversions

Definitions

a. Petroleum hydrocarbons focused upon in this analysis

For the purposes of estimating the input of petroleum hydrocarbons to marine environment, some consideration was given to the nature of this complex group of compounds. The estimates included here are intended to be as inclusive as possible (see individual sections for greater explanation of how various classes of hydrocarbons were treated); however, the committee found it practical and pragmatic to focus its attention on liquid petroleum compounds of higher molecular weights (i.e., methane, ethane, and other compounds lighter than C_6 are not included in the calculated estimates).

b. North American waters and specific regions of study

In analyzing oil-input data from all sources around North America, the committee determined that there would be some value to compiling that data according to certain discrete geographic boundaries, based primarily on the influence of major estuaries and marine water circulation patterns in each area. To the extent possible, boundaries selected also recognize the operational boundaries between various U.S. Coast Guard offices. This should enable more efficient comparison of inputs between regions around the United States as an aid in focusing control efforts.

Boundaries were established as follows around the North American coast:

1. Nearshore: from the shore along the coastline seaward 3 miles to the demarcation line between state and federal waters, except in estuaries (bays, sounds, river mouths, etc.), where input data will be collected inland to include all tidally affected waters (i.e., to the extent those waters remain navigable to ocean-going commercial, self-propelled vessels).
2. Offshore: from the 3-mile demarcation line out to the outer limit of the Economic Exclusion Zone (EEZ) generally 200 miles from shore.

c. Units Used and Conversion Factors

Lateral boundaries were also established to distinguish between regions around the coast based on political boundaries (between Canada, the United States, and Mexico) and between certain Coast Guard operational unit boundaries within the United States based on major estuaries within those boundary areas (see Figure 1-7 and Table B-1).

Barrels	× 42	= US gallons
Liters	× 0.264	= US gallons
Cubic meters	× 264.2	= US gallons
Cubic feet	× 7.481	= US gallons
Liters	× 0.0009	= Tonnes* (note tonnes = metric tons)
Tonnes	× 294	= US gallons*
U.S. gallons	× 0.0034	= Tonnes*

*Note: The gallon is a volume measurement. The tonne is a weight measurement. For truly precise conversions between gallons and tonnes, it is important to take into account that equal volumes of different types of oil differ in their densities. The specific gravity (sp gr), or density in relation to pure water is generally less than 1.0. Specific gravity of petroleum products varies from about 0.735 for gasoline to about 0.90 for heavy crude to 0.95 for Bunker C (No. 6 fuel). In some cases the oil is even heavier than water, especially with some of the heavy No. 6 fuels. These oils can sink. The

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volume that a particular weight of oil takes up varies with temperature and atmospheric pressure.

The conversion factor of 294 gallons per tonne is derived from an average specific gravity of 0.83, which corresponds to an API gravity or degree API of 39. Note that API gravity and specific gravity are inversely proportional as per the formulae below. The 294 gallons/tonne conversion unit is also convenient because it happens that 294 gallons = 7 barrels.

API = (141.5/sp gr) – 131.5

sp gr = 141.5/(API + 131.5)

TABLE B-1 Descriptions of Coastal Zones as Defined by This Study

Zone	Description
A	Bounded by a line drawn northerly 0° true along the U.S./Canada border in the Arctic and a line bearing northerly 0° true from Lancaster Island in Canada (includes Arctic Canada west of Hudson Bay).
B	Bounded by a line bearing northerly 0° true from Lancaster Island in Canada and a line bearing easterly 90° true from the northern boundary of Newfoundland, Canada (includes Hudson Bay east to the Maritime Provinces in Canada).
C	Bounded by a line bearing easterly 90° true from the northern boundary of Newfoundland, Canada, and a line drawn easterly along the U.S./Canada border as follows: a line drawn 90° true from the shore along 44°11'12" N to 67°16'46" W; thence southwest to 42°53'14" N, 67°44'35" W; thence southeast to 42°31'08" N, 67°28'05" W; thence southeast to 40°27'05" N, 65°41'59" W.
D	Bounded by a line drawn easterly along the U.S./Canada border and a line bearing due east 90° true from the shore at the Virginia/North Carolina border (34°59.8' N) to the offshore extent of the EEZ [includes US Coast Guard Marine Safety Offices (MSOs) Portland, Maine; Boston; Providence; Long Island Sound, Connecticut; New York; Philadelphia; Baltimore; and Hampton Roads, Virginia].
E	Bounded by a line bearing due east 90° true from the shore at the Virginia/North Carolina border (34°59.8' N) to the offshore extent of the EEZ and by a line bearing 227° true drawn from 26°00' N latitude and 81°30' W longitude to the offshore extent of the EEZ (includes MSOs Charleston, Savannah, Jacksonville, and Miami).
F	Bounded by a line bearing 227° true drawn from 26°00' N latitude and 81°30' W longitude to the offshore extent of the EEZ and a line from the Mississippi coast at 89°10' W bearing southeasterly to 29°10' N, 88°00' W; thence southerly bearing 180° true to the offshore extent of the EEZ (includes MSOs Tampa Bay and Mobile).
G	Bounded by a line from the Mississippi coast at 89°10' W bearing southeasterly to 29°10' N, 88°00' W; thence southerly bearing 180° true to the offshore extent of the EEZ and a line drawn along the U.S./Mexico boarder in Texas bearing 90° true to the offshore extent of the EEZ (includes MSOs New Orleans and Morgan City, Louisiana; and Port Arthur, Houston and Corpus Christi, Texas).
H	Includes Mexican offshore waters on the east coast of Mexico that are south of a line bearing 90° true from the U.S./Mexico border to the outermost extent of the EEZ and north of a line bearing 90° true from the Mexico/Belize border to the outermost extent of the EEZ.
I	Includes the areas of both the Commonwealth of Puerto Rico and the Territory of the U.S. Virgin Islands to the offshore extent of the EEZ (includes MSO San Juan).
J	Includes Mexican offshore waters on the west coast of Mexico that are south of a line bearing 270° true from the U.S./Mexico border to the outermost extent of the EEZ and north of a line bearing 270° true from the Mexico/Guatemala border to the outermost extent of the EEZ.
K	Includes a line along the U.S./Mexico border in California to the offshore extent of the EEZ and a line drawn from the intersection of 34°58' N latitude and the California coastline bearing 229° true to the offshore extent of the EEZ (includes MSOs San Diego and Los Angeles/Long Beach).
L	Includes a line drawn from the intersection of 34°58' N latitude and the California coastline bearing 229° true to the offshore extent of the EEZ and a line drawn along the 42°00' N latitude from the shore to the offshore extent of the EEZ (includes MSO San Francisco).
M	Includes a line drawn along the 42°00' N latitude from the shore to the offshore extent of the EEZ and a line drawn along the international boundary between the United States and Canada at the entrance to the strait of Juan de Fuca to the offshore extent of the EEZ (includes MSOs Portland, Oregon, and Puget Sound, Washington).
O	Includes a line drawn along the international boundary between the United States and Canada at the entrance to the strait of Juan de Fuca to the offshore extent of the EEZ (48°29'38.11" N, 124°43'34.69" W to 48°29'38.11" N, 125°00'00" to 48°04'00"N, 126°10'35" W) and a line along the international boundary bearing 270° true between the United States and Canada at the Dixon entrance to the offshore extent of the EEZ (includes all marine waters in western Canada.)
N	Includes Hawaii, American Samoa, Johnston Atoll, Palmyra Atoll and Kingman Reef, Wake Island, Jarvis Island, Howland and Baker Islands, Guam, the Commonwealth of Northern Mariana Islands, and the Trust Territory of the Pacific Islands.
P	Includes a line drawn along the international boundary bearing 270° true between the United States and Canada at the Dixon entrance to the offshore extent of the EEZ and a line drawn along the northern edge of the Aleutian Island chain to the offshore extent of the EEZ (includes MSO Southeast Alaska and a portion of MSO Western Alaska).
Q	Includes a line drawn along the northern edge of the Aleutian Island chain to the offshore extent of the EEZ and a line drawn northerly 0° true along the U.S./Canada border in the Arctic.

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C

Natural Seepage of Crude Oil into the Marine Environment

Crude oil spills in the marine environment, if sufficiently large, often lead to serious environmental pollution, but environmental pollution can also be caused by natural seepage of crude oil. This latter case results in environmental contamination. Estimating the amount of natural seepage of crude oil into the marine environment involves broad extrapolations from minimal data. The National Research Council (1975, 1985) has made these kinds of estimates previously, and what follows in an update of this information. Because of the nature of these estimates, they are normally reported to one significant figure (best estimate and range of estimates), except when quoted from cited references. The units used are metric tons (tonnes).

RECENT ESTIMATES OF SEEPS IN THE NORTHERN GULF OF MEXICO

Recent studies have suggested that seepage rates in the Gulf of Mexico are much higher than reported in previous NRC studies (1975, 1985). MacDonald et al., (1996) using submarines and remote sensing have identified at least 63 individual seeps (Fig. 2-11). For example, using satellite remote sensing to map oil slicks, MacDonald et al. (1993) estimated the total seepage in a region of about 23,000 km^2 in the Gulf to be about 17,000 tonnes per year. Later, however, MacDonald (1998) conservatively estimated a much lower rate of about 4,000 tonnes per year as a minimum. The difference in these estimates results from the various underlying assumptions that have been used and emphasizes the difficulty in establishing seepage rates. These estimates have now been revised based on SAR and other remote sensing data, compiled by commercial enterprises (Earth Satellite Corporation and Unocal Corporation). With the Earth Satellite data set, Mitchell et al. (1999) estimated oil seepage rates ranging from about 40,000 to 100,000 tonnes per year, with an average rate of 70,000 tonnes per year. This value accounts only for the northern Gulf of Mexico and excludes the Campeche Basin offshore from Mexico, one of the more prolific petroleum basins in the world. Assuming the seep scales are proportional to the surface area, a reasonable seep rate for the entire Gulf is about double the northern Gulf estimate, giving a total Gulf of Mexico seep rate of about 140,000 tonnes per year (ranging from 80,000 to 200,000 tonnes per year).

However, because of the assumptions made during interpretation of the satellite information, a number of uncertainties exist, including:

1. An assumed mean thickness of 0.1mm for the surface slick thickness. This value is largely based on arguments of MacDonald et al., (1993), who considered threshold thicknesses of 0.1 and 0.01 mm. The slick thickness, of course, affects the total volume estimate in a linear way.
2. A mean residence time on the surface of 12 hrs. This value is also based on work by MacDonald et al., (1993), who noted abrupt changes observed in wind and slick patterns. They estimate a reasonable range of residence times between 8-24 hr, which affects the total seep rates linearly.
3. The seep rate over a large region is constant in time. MacDonald et al., (1993, 2000) and others have noted that some seeps are episodic and ephemeral. Hence, assuming constant rates, even when integrated over a large region, may be questionable.

RECENT ESTIMATES OF SEEPS OFF SOUTHERN CALIFORNIA

Natural oil seeps have been noted offshore of southern California in the past (Weaver, 1969; Yerkes et al., 1969), and their distribution is extensive. Early rates were measured using primitive techniques and extensive extrapolations. For example, at Coal Oil Point, early estimates ranged from 520

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to 8,300 tonnes per year (Mikolaj et al., 1972; Wilkinson, 1971). Straughen and Abbott (1971) estimated 4,700 tonnes per year (when corrected for a printing error, pointed out in Kvenvolden and Harbaugh, 1983). In Santa Monica Bay, seep estimates by Mikolaj et al., (1972) and Wilkinson (1971) range from 100 to 1,000 tonnes per year. Estimates by Fischer (1978), based on mapping of the geographical trends of seeps in the Santa Barbara Channel, range from 2,100 to 35,000 tonnes of oil per year.

Recently, more accurate measurements have become available in the Coal Oil Point region from Clester et al., (1996) and Hornafius et al., (1999). They combined information from 'seep tents' (funnel-like structures placed over natural seeps), seep-flux buoys that drifted across the seep region, and 50 kHz sonar date. They concluded that Coal Oil Point seeps about 7,800 to 8,900 tonnes of oil per year. To account for seeps likely to be present elsewhere in the Santa Barbara Channel and the offshore Santa Maria and Santa Monica Basins, the total oil seepage offshore southern California is now estimated to be about twice the seepage at Coal Oil Point, or about 17,000 tonnes annually, rounded to one significant figure of 20,000 tonnes of oil per year. This estimate is large but is still less than the upper estimate of Fischer (1978) of 35,000 tonnes per year.

SEEPAGE ESTIMATES FOR THE NORTH AMERICAN OFFSHORE

There are four regions offshore North America with known seeps. Two of these, the Gulf of Mexico and southern California, have a combined annual oil seep rate of 160,000 tonnes, derived by adding 140,000 tonnes, estimated from the Gulf of Mexico, and the estimate of 20,000 tonnes from Southern California. Seeps are also known to be present along the northern and southern coastlines of Alaska (Fig. 2-13) and at the coastline of Baffin Island, Canada.

Becker and Manen (1988) identified 29 seeps within the coastal regions of Alaska (Fig. 2-13). Of the 29 areas, 14 are confirmed as actual oil seeps and 15 are unconfirmed reports from the shoreline of the Gulf of Alaska. None of the seeps are beneath the water surface. Rather they lie above the low-tide line or at inland sites and could influence the marine environment through oil transport in freshwater streams.

Using the mean values gives a total of about 360 tonnes annually. Recently, Page et al. (1997) suggested that the total seepage rate from onshore and offshore seep sources into the eastern Gulf of Alaska is much greater than 400 to 1,200 tonnes per year; howevr, they did not specify an upper limit, and included both free petroleum and extractable organic material of sediments in their estimates. Although submarine oil seeps offshore from Alaska have been suspected, there are no documented reports in the public record (Becker and Manen, 1988). Because the seeps of Alaska have not been fully documented, and in order to account for probable undiscovered seeps, the seepage rate for Alaska is conservatively estimated to be 400 tonnes annually.

In Canada, oil seeps have been found at Scott Inlet (Levy, 1978) and Buchan Gulf (Levy and Ehrhardt, 1981) on Baffin Island. Although the evidence shows that oil is seeping from the seabed, no rates of oil seepage have been measured or estimated.

Tables 2-5 through 2-9 summarize the estimates of the yearly amounts of oil seepage occurring offshore from North America. The total seepage is 160,000 tonnes per year. The new estimate seems reasonable given the relative percentage of potential oil-producing areas in North America compared with the rest of the world. In addition, recent remotely-sensed data suggest that North America is by no means an exceptional region for seeps.

GLOBAL ESTIMATES OF OIL SEEPAGE INTO THE MARINE ENVIRONMENT

Considering that totally different approaches were taken to estimating global oil seepage rates, it is remarkable that the 'best estimates' obtained by Wilson et al. (1973, 1974) of 600,000 tonnes per year (National Research Council, 1975) and by Kvenvolden and Harbaugh (1983) of 200,000 tonnes per year (National Research Council, 1985) fall within a factor of three of each other. Whereas Wilson et al. (1973a,b) established plausible, but not likely accurate rates for current conditions, Kvenvolden and Harbaugh (1983) determined possible average rates throughout geologic time and established constraints on these rates based on the availability of oil for seepage. In a sense, the two approaches complement each other, one establishing reasonable rates and the other reasonable limits.

Nevertheless, recent and improved data from the northern Gulf of Mexico and from offshore southern California indicate that oil seepage rates were likely underestimated in 1985 (National Research Council, 1985). Based on the above information and using the methods of Kvenvolden and Harbaugh (1983), the annual global oil seepage rate is now estimated to be between 200,000 and 2,000,000 tonnes (60 and 600 million gallons). The 'best estimate' of 600,000 tonnes (180 million gallons), within this range, comes from the acceptance of the original estimates of Wilson et al. (1973, 1974), resulting from a new appreciation for the magnitude of the natural seepage of crude oil, particularly in the Gulf of Mexico.

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D

Oil and Gas Extraction

ACCIDENTAL DISCHARGE FROM PLATFORMS

Volumes of petroleum hydrocarbons introduced into North American waters from accidental discharge on offshore platforms are relatively well known for the U.S. Outer Continental Shelf and Canada, but data from offshore Mexico and coastal waters in the United States are generally lacking. Data bases used in this report include the Minerals Management Service Spill Data Base, the 1999 PEMEX Safety, Health and Environmental Report, Canadian Environmental Report, and data on pipeline spills in coastal waters are from the U.S. Coast Guard (see detailed discussion of spill data used, available at http://www4.nationalacademies.org/dels/oilannex.nsf).

Table D-1 lists the amount of petroleum hydrocarbons spilled into the sea in the offshore waters from 1990 to 1999. A total of 149 spills occurred during this ten year period, discharging some 556 tonnes into marine waters. Of the 556 tonnes spilled in the past ten years, eighteen accidental spills in 1995 account for nearly a third of the total. The average annual amount discharged in offshore waters, based on the MMS data base, is 55.6 tonnes per year. Removing a few non-hydrocarbon spills from this data base and adding additional spills from the U.S. Coast Guard data base resulted in an average calculated discharge of 57.0 tonnes per year.

Platform discharges in other North American waters were somewhat more difficult to obtain as data bases were not systematically collected during the past decade. In Canadian east coast waters, a total of 280 tonnes has been spilled into the sea during the period 1990 through 1999 (Table D-2), resulting in an average annual discharge of 28.0 tonnes

TABLE D-1 Summary of Outer Continental Shelf (U.S.) Data Base of Oil and Gas Facilities Spill Data, 1990-1999

Annual Oil Spillage From Offshore Platforms in US Waters (1990-1999)

Year	Number Spills (>100 gal)	Tonnes Spilled	Gallons Spilled	Avg. Spill Size (Tonnes)	Avg. Spill Size (Gallons)
1990	18	26.66	7,510	1.48	417
1991	17	72.75	19,996	4.28	1,176
1992	12	36.45	10,500	3.04	875
1993	6	5.40	1,470	0.90	245
1994	18	50.39	14,083	2.80	782
1995	18	175.73	54,696	9.76	3,039
1996	20	52.95	15,038	2.65	752
1997	12	44.47	13,291	3.71	1,108
1998	16	46.25	12,865	2.89	804
1999	12	45.15	12,983	3.76	1,082
Total	149	556.20	162,432	3.53	1,028

SOURCE: Minerals Management Service; Analysis by Environmental Research Consulting

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TABLE D-2 Summary of Oil and Gas Facilities Spill Data for the East Coast of Canada, 1990-1999

	Total Spillage	
Year	Tonnes	U.S. Gallons
1990	0.0	0
1991	0.0	0
1992	13.4	3,948
1993	2.6	756
1994	2.9	840
1995	248.5	7,308
1996	1.6	462
1997	4.0	1,176
1998	6.4	1,890
1999	1.0	294
Ave.	28.0	1,667.4
Max.	248.5	7,308
Min.	0.0	0.0

(8,200 gallons). The number of platforms existing in offshore Mexican waters is relatively small, but in U.S. coastal waters, there are a significant number of shallow-water platforms, especially in the northern Gulf of Mexico. Approximately 877 petroleum facilities were located in U.S. coastal waters in 1992 (Federal Register, December 16, 1996, p.66089). Using scattered data bases from the U.S. Coast Guard, several state reports, and estimating the number of offshore platforms in Mexican waters (130 platforms), a calculated volume of 61.0 tonnes (18,000 gallons) appear to be a reasonable estimate of discharge from these facilities. Thus, in North American coastal waters, a total annual load discharged is calculated at 89.0 tonnes per year (28.0 tonnes in Canadian waters plus 61.0 tonnes in other coastal waters).

Thus, an estimated total of 146.0 tonnes have been discharged annually into North American waters by accidental spills and blowouts from offshore oil and gas facilities in U.S.offshore., U.S. coastal waters, Canadian and Mexican waters. Tables 2-2 through 2-6 includes annual average petroleum hydrocarbon load from accidental discharges, reported between 1990 and 1999, from offshore oil and gas facilities in the four zones where reliable data was available. These average annual loads were calculated from accidental discharges reported in a known latitude and longitude (and thus represent a subset of the numbers reported in Table D-3). Note that in Tables 2-2 through 2-6, that approximately 90% of the total discharges from production facilities occurred in Zone G (central and western Gulf of Mexico) and of that amount, nearly 50% was within coastal waters.

SPILLS FROM OFFSHORE PIPELINES

Pipeline spill data for North American waters were obtained from two data sets: U.S. Coast Guard and the Minerals Management Service. Table D-4 shows the total and average pipeline spills from 1990 through 1999 in offshore North American waters (MMS data base). Additional spills, as determined from the U.S. Coast Guard data base, resulted in a calculated annual volume of discharged petroleum hydrocarbons in offshore waters to be 59.0 tonnes. In coastal waters, the only reliable data was from the U.S. Coat Guard data base (Table D-5). The data base, however, included spills from facilities and contained non-crude spills. These were removed, and a calculated volume of 1,100 tonnes per year was calculated. It is estimated that there are 23,236 miles of pipelines in offshore North American waters (DeLuca and Leblanc, 1997), thus the average accidental discharge per mile of pipeline would be 0.074 tonnes per pipeline mile. These calculations do not include spills from pipelines in Mexico as the data was not available. The number and length of pipelines in Mexico are relatively small when compared to those in the United States and it is though that the volume spilled is proportionate. Canadian data was available, but no discharges were reported. Using these scattered data bases, an annual total discharge into Norh American waters by accidental spills from pipelines is calculated to be 1,690 tonnes per year.

Offshore Oil and Gas Production and Pipeline Spill Summary

Thus, the total documented average volume of petroleum hydrocarbons accidentally discharged from offshore facilities (platforms and pipelines) per year into North American waters during the past decade is 1,836 tonnes (Tables D-3 and Tables 2-2 through 2-6).

INTERNATIONAL SPILLS FROM PLATFORMS AND PIPELINES

Internationally, the amount of petroleum introduced to the sea from oil/gas production and pipeline spills and blow-

TABLE D-3 Summary of Calculated Inputs from Offshore Oil and Gas Facilities for North American and Worldwide Waters

	North American Waters	Other Waters Worldwide	Total
Oil/Gas Production Facilities	146.0 tonnes	144.0 tonnes	290.0 tonnes
Pipeline Spills	1,690.0 tonnes	4,410.0 tonnes	6,100.0 tonnes
Total	1,836.0 tonnes	4,554.0 tonnes	6,390.0 tonnes

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TABLE D-4 Summary of Offshore Pipeline Spill Data for North American Waters, 1990-1999

Annual Oil Spillage From Offshore Pipelines in US Waters (1990-1999)

Year	Number Spills (>100 gal)	Tonnes Spilled	Gallons Spilled	Avg. Spill Size (Tonnes)	Avg. Spill Size (Gallons)
1990	9	2,621.15	779,882	291	86,654
1991	19	22.89	6,300	1	332
1992	9	319.97	86,730	36	9,637
1993	7	13.72	3,780	2	540
1994	2	599.74	190,684	300	95,342
1995	4	4.96	1,344	1	336
1996	4	25.65	6,952	6	1,738
1997	8	6.11	1,693	1	212
1998	6	1,559.60	430,214	260	71,702
1999	7	500.34	135,611	71	19,373
Total	75	5674.13	1,643,190	97	28,587

SOURCE: Minerals Management Service; Analysis by Environmental Research Consulting

outs is even harder to estimate as data is even more difficult to acquire. As of 1993, there were 3,182 additional offshore oil and gas facilities located in non-North American waters (International Association of Oil and Gas Producers, 2000). If it assumed that the average amount of petroleum hydrocarbons spilled by these platforms was similar to those found in North American waters, the estimated additional average spill volume would be 115.0 tonnes per year (0.036 tonnes per platform per year). Comparison of this calculation with scattered data from the North Sea and offshore Africa tended to indicate that the computed figure was extremely low. Using the data cited above, an average of 0.045 tonnes per platform (reflecting a 25 percent increase in the per platform release rate[1]) was used to compute the volume discharged into the sea by non-North American platforms. The resulting computed value is 144.0 tonnes per year. It is the opinion of the committee that this number is still low, but until more systematic data is collected worldwide on discharges from platforms, a more precise volume is lacking. Thus, on an annual basis, an estimated 290.0 tonnes are spilled into the world's oceans by all offshore oil and gas platforms (Table D-3).

DeLuca and LeBlanc (1997) estimate that there are 59,512 miles of offshore oil and gas pipelines in the major oil producing countries of the world (North America not included). Again, this number is probably too low by as much as 30%, but these are the only published figures available. If it is assumed that the average amount of petroleum hydrocarbons discharged per mile of pipeline in North America is (0.074 tonnes per year per pipeline mile), then an additional 4,410 tonnes are discharged into the other world's oceans by non-North American pipelines. Thus, on an annual basis,

[1]Assuming that non-North American platforms release 25 percent more petroleum per year is a somewhat subjective figure, but reflects the lack of worldwide standards. In other words, while some regions set standards as high as North American producers operate under, these standards are not uniformly applied worldwide. Thus, the adjustment is conservative in that it reflects the assumption that less regulated operations are more prone to release petroleum.

TABLE D-5 Summary of Pipeline Spill Data in North American Coastal Waters, 1990-1999

		Tonnes		U.S. Gallons	
Year	No. Spills	Total	Ave./Spill	Total	Ave./Spill
1990	25	2,919.99	116.80	791,317	31,653
1991	5	1,095.85	219.17	296,975	59,395
1992	22	1,010.06	45.91	273,726	12,442
1993	11	1,438.91	130.81	389,945	35,450
1994	22	11,344.55	515.66	3,074,373	139,744
1995	13	53.97	4.15	14,626	1,125
1996	19	3,670.65	193.19	994,746	52,355
1997	10	1,401.77	140.18	379,880	37,988
1998-1999	17	530.14	31.18	143,668	8,451
Total	144	23,465.89		6,359,256	
Ave./Year	16	2,607.32		706,584	

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6,100 tonnes per year of petroleum hydrocarbons are discharged into the world's oceans by pipeline spills.

Using the estimates cited above, the total amount of petroleum hydrocarbons discharged into the world's oceans by offshore oil and gas facilities is 6,390 tonnes per year (290.0 tonnes—platforms; 6,100.0 tonnes—pipelines; Table D-3).

ESTIMATES OF VOLATILE ORGANIC COMPOUND

Introduction

During the production, transport, and refining of hydrocarbons, volatile compounds escape to the atmosphere. Some, like methane, are light and rise or degrade rapidly. Heavier compounds, like hexadecane, react or rise more slowly. These heavier hydrocarbons are labeled as volatile organic compounds (VOC) and are defined in the U.S. Clean Air Act to include all volatile hydrocarbons except methane, ethane, a wide range of chlorofluorocarbons (CFC), hydrochloroflourocarbons (HCFC), and a few others, e.g., acetone. A complete listing of the constituents is given in Table D-6. Unfortunately the definition provides no exact ratio of carbon to compound. As a practical definition, the list contains most compounds above propane (C_3H_8, 82 percent carbon) and below hexadecane ($C_{16}H_{34}$, 85 percent carbon).

The focus of this section is on estimating the amount of VOC generated from offshore production platforms. Sections B and C include estimates of VOC generated during tanker transport and marine terminal loading. The estimates exclude other potential sources of VOC released from coastal or near-river refineries, storage tanks, etc.

Prior to 1990, VOC from production platforms received little attention and no estimates were provided by NRC (1985, 1975) or GESAMP (1993). One reason is that VOC data just started to appear in the late 1980s. Another reason is that the overall contribution to the sea was thought to be small. That's in part because the scavenging of VOC from the atmosphere to the sea is inefficient and highly dispersed. At most a few percent of VOC ever make it to the sea, and these are spread over a large area compared to the scale of the generation source.

General Methodology

While data collection on VOC has improved, it remains crude and sparse on a worldwide basis. Regulators have made estimates for the U.S. Gulf of Mexico (offshore) and California. These estimates are not actual measurements but are calculated usually from an inventory of equipment multiplied by an estimated VOC emission rate for each piece of equipment. Producers have made estimates for the Mexican Gulf of Mexico and the producing basins of the northeast Atlantic (North Sea, Norwegian Sea, etc.), but documentation of their methods could not be found. In all cases, there is no information on the uncertainty in their estimates or speciation (percent occurrence of each compound) of the VOC, an important factor when considering how much of the VOC might make it back to the sea or what its toxic effect might be. Still, the situation in the above regions is better then the other offshore producing areas where no estimates were found.

Oil and Gas Producers (1994) describes four methods for estimating VOC (and other emissions) from offshore operations. The simplest, Tier 1, estimate is based on total production volume and tends to be conservative. Developing the higher tier estimates requires details concerning platform-specific oil types, fuel consumption, equipment, etc. Since there are thousands of offshore facilities and no central databases, it would be a daunting task to apply these higher tier methods on a worldwide basis or even for North America. MMS has required the Gulf of Mexico operators to provide a Tier 3 estimate by the summer of 2001 but not in time for this report.

For the reasons cited above, the Tier 1 method was used in this report. It requires an estimate of the production volume and a VOC rate per unit produced. E&P Forum (1994) provides estimates based on the information available at the time but a review of the literature revealed more recent and detailed information.

Table D-6 shows the VOC rate for the four regions where VOC estimates have been made. The source of these numbers is given in later discussions. The average of the rates is given in the last row. Mexico (Pemex, 2000) has reported the lowest rate, which was roughly five times lower then in the northeast Atlantic and nearly three times lower then in the U.S. Gulf of Mexico. The smallness of the Mexican number was surprising especially when compared to the U.S. Gulf numbers where oil types were similar and production methods are likely to be at least as clean. Unfortunately no insight was offered into how the Mexican number was calculated so it was difficult to determine the source of the difference. Consequently we took the Mexican rate at face value.

It is of some interest to compare the E&P Forum (1994) VOC rates to those in Tables 2-2 through 2-6. The E&P rate for the N. E. Atlantic of 1.1×10^{-3} (based on an average of the E&P values for Norway and the U. K.) compares well to the 1.17×10^{-3} developed in this study. The only other common region is the Gulf of Mexico. Here the E&P estimate of 2.2×10^{-3} is about four times larger then developed in this study. The source of the discrepancy is fairly obvious: E&P based their estimates on an EPA estimate that was not as recent as the MMS estimates used in this study. E&P also provides estimates for Canada but these are based on onshore fields in Alberta, not a particularly good basis.

The lowest VOC rate in Tables 2-2 through 2-6 was used to estimate the lower bound estimate of VOC for each region, and the highest VOC rate was used to estimate the upper bound estimate. For regions where no VOC were published, the best estimate of VOC emissions was calculated by multiplying the average in Tables 2-2 through 2-6 by the

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TABLE D-6 Hydrocarbon Compounds Considered VOC by the EPA Interpretation of the U.S. Clean Air Act (40 CFR 51.100)

(s) *Volatile organic compound (VOC)* means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions.

1.) This includes any such organic compound other than the following, which have been determined to have negligible photochemical reactivity:

- methane
- ethane
- methylene chloride (dichloromethane)
- 1,1-trichloro-ethane (methyl chloroform)
- 1,1,2-trichloro-1,2,2-trifluoroethane (CFC– 113)
- trichlorofluoromethane (CFC–11)
- dichlorodifluoromethane (CFC–12)
- chlorodifluoromethane (HCFC–22)
- trifluoromethane (HFC–23)
- 1,2-dichloro 1,1,2,2-tetrafluoroethane (CFC–114)
- chloropentafluoroethane (CFC–115)
- 1,1,1-trifluoro 2,2-dichloroethane (HCFC–123)
- 1,1,1,2-tetrafluoroethane (HFC–134a)
- 1,1-dichloro 1-fluoroethane (HCFC–141b)
- 1-chloro 1,1-difluoroethane (HCFC–142b)
- 2-chloro-1,1,1,2-tetrafluoroethane (HCFC–124)
- pentafluoroethane (HFC–125)
- 1,1,2,2-tetrafluoroethane (HFC–134)
- 1,1,1-trifluoroethane (HFC–143a)
- 1,1-difluoroethane (HFC–152a)
- parachlorobenzotrifluoride (PCBTF)
- cyclic, branched, or linear completely methylated siloxanes
- acetone
- perchloroethylene
- tetrachloroethylene
- 3,3-dichloro-1,1,1,2,2-pentafluoropropane (HCFC– 225ca)
- 1,3-dichloro-1,1,2,2,3-pentafluoropropane (HCFC–225cb)
- 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC 43–10mee)
- difluoromethane (HFC–32)
- ethylfluoride (HFC–161)
- 1,1,1,3,3,3-hexafluoropropane (HFC–236fa)
- 1,1,2,2,3-pentafluoropropane (HFC–245ca)
- 1,1,2,3,3-pentafluoropropane (HFC–245ea)
- 1,1,1,2,3-pentafluoropropane (HFC– 245eb)
- 1,1,1,3,3-pentafluoropropane (HFC–245fa)
- 1,1,1,2,3,3-hexafluoropropane (HFC–236ea)
- 1,1,1,3,3-pentafluorobutane (HFC–365mfc)
- chlorofluoromethane (HCFC–31)
- 1 chloro-1-fluoroethane (HCFC–151a)
- 1,2-dichloro-1,1,2-trifluoroethane (HCFC–123a)
- 1,1,1,2,2,3,3,4,4-nonafluoro-4-methoxy-butane (C4F9OCH3)
- 2-difluoromethoxymethyl-1,1,1,2,3,3,3-heptafluoropropane (Cf3)2CFCF2OCH3)
- 1-ethoxy-1,1,2,2,3,3,4,4,4-nonafluorobutane (C4F9OC2H5)
- 2-(ethoxydifluoromethyl)-1,1,1,2,3,3,3-heptafluoropropane (CF3)2CFCF2OC2H5)
- methyl acetate
- perfluorocarbon compounds that fall into these classes:
  - i.) Cyclic, branched, or linear, completely fluorinated alkanes;
  - ii.) Cyclic, branched, or linear, completely fluorinated ethers with no unsaturations;
  - iii.) Cyclic, branched, or linear, completely fluorinated tertiary amines with no unsaturations; and
  - iv.) Sulfur containing perfluorocarbons with no unsaturations and with sulfur bonds only to carbon and fluorine.

2.) For purposes of determining compliance with emissions limits, VOC will be measured by the test methods in the approved state implementation plan (SIP) or 40 CFR, part 60, Appendix A, as applicable. Where such a method also measures compounds with negligible photochemical reactivity, these negligibly reactive compounds may be excluded as VOC if the amount of such compounds is accurately quantified, and the enforcement authority approves such exclusion.

3.) As a precondition to excluding these compounds as VOC or at any time thereafter, the enforcement authority may require an owner or operator to provide monitoring or testing methods and results demonstrating, to the satisfaction of the enforcement authority, the amount of negligibly reactive compounds in the source's emissions.

4.) For purposes of federal enforcement for a specific source, the EPA shall use the test methods specified in the applicable EPA-approved SIP, in a permit issued pursuant to a program approved or promulgated under title V of the Act, or under 40 CFR, part 51, Subpart I or Appendix S, or under 40 CFR, parts 52 or 60. The EPA shall not be bound by any state determination as to appropriate methods for testing or monitoring negligibly reactive compounds if such determination is not reflected in any of the above provisions.

5.) As discussed more fully in Appendix H, ignoring the substantial atmospheric reactions and using the physical properties of decane result in a very conservative calculation, likely overestimating hydrocarbon loadings to the oceans from these sources. Under this simple scenario, equilibrium calculations show that less than 0.2 percent of the released VOC are deposited to surface waters, even under these very conservative conditions. Thus the values reported in Chapters 2 and 3 are 0.2 percent of the estimated mass released reported in Table D-7.

volume of oil produced in the region. Otherwise the published VOC rates were used to calculate the best estimate of VOC emissions.

When viewing the tables in this section, it should be kept in mind that these are total estimated VOC released to the atmosphere. These estimates will later be used in Section E to estimate the total VOC going back to the sea.

North American Estimates

Table D-7 summarizes the estimated VOC emissions for producing platforms in the various zones of North America. Five columns are shown for each zone. Columns 2-4 show the lower, best, and upper limits of the estimated annual tonnage of VOC discharged to the atmosphere. Column 5 shows

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TABLE D-7 Estimates of VOC (Kilotonnes/yr) Released and Offshore Oil Produced (Kilotonnes/yr) in North America during 1995

Offshore Air Emissions (VOC, k-tons per year)						Offshore	
Zone	>10%	50%	<-90%	Oil Produced (k-tons/yr)	Source	Oil Production Rate (kbbl/day)	Description of Region
A > 3 mi	0	0	0	0		0	Canadian Arctic west of Hudson Bay
A < 3 mi	0	0	0	0			
B > 3 mi	0	0	0	0		0	Canadian Arctic east of Hudson Bay
B < 3 mi	0	0	0	0			
C > 3 mi	0	0	0	0		0	Canadian Maritime provinces
C < 3 mi	0	0	0	0			
D > 3 mi	0	0	0	0		0	Maine to Virginia
D < 3 mi	0	0	0	0			
E > 3 mi	0	0	0	0		0	N. Carolina to Florida Straits
E < 3 mi	0	0	0	0			
F > 3 mi	0	0	0	0	API XI-15		Eastern GOM (MI and east)
F < 3 mi	0	0	0	0	API XI-15		
G > 3 mi	9	28	59	50,410	API XI-15	942	Western GOM (LA & west)
G < 3 mi	1	2	5	4,422	API XI-15	83	
H > 3 mi	22	22	138	117,742	PEMEX 1999 Annual report	2,200	Campeche
H < 3 mi	0	0	0	0			
I > 3 mi	0	0	0	0		0	West coast of Mexico
I < 3 mi	0	0	0	0			
J > 3 mi	2	3	12	10,621	API XI-15	198	S. California
J < 3 mi	1	1	3	2,907		54	
K > 3 mi	0	0	0	0		0	N. California
K < 3 mi	0	0	0	0			
L > 3 mi	0	0	0	0		0	Oregon/WA coast
L < 3 mi	0	0	0	0			
M > 3 mi	0	0	0	0		0	Western Canada
M < 3 mi	0	0	0	0			
N > 3 mi	0	0	0	0	API XI-15		SE Alaska including Cook Inlet
N < 3 mi	1	4	8	6,919	API XI-15	129	
O > 3 mi	0	0	0	0		0	Bering, Chukchi, Beaufort Seas
O < 3 mi	0	0	0	0			
P > 3 mi	0	0	0	0		0	Puerto Rico, Virgin Is.
P < 3 mi	0	0	0	0			
Q > 3 mi	0	0	0	0			
Q < 3 mi	0	0	0	0		0	Hawaii, W. Pacific
North America	36	60	226	193,020		3,607	
W. Europe	41	254	381	216,859	API XI-2	4,052	
Africa	30	88	188	160,718	API XI-2	3,003	
Middle East	34	99	211	180,520	API XI-2	3,373	
S. America	10	29	62	53,412	API XI-2	998	
Asia & Pacific	38	113	240	205,513	API XI-2	3,840	
E. Europe/Russia	2	6	13	11,185	API XI-2	209	
World Wide Total	191	649	1,322	1,214,247		19,082	

	VOC(ton)/oil(k-ton)/yr	VOC(k-ton/yr)/Oil(kbbl/day)
Calif VOC/kbbl=	2.80E-04	0.015
GOM VOC/kbbl=	5.61E-04	0.030
PMEX=	1.87E-04	0.010
UK/Norway VOC/kbbl=	1.18E-03	0.063
avg=	5.42E-04	0.029

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the estimated annual tonnage of offshore oil produced for the year 1995 from API (2001). The year 1995 was the most recent year included in API (2001). Note that most of the rows are "zero" because there is no offshore production in those zones in 1995.

Estimates for VOC rates in the U. S. Gulf of Mexico come from the Minerals Management Service (MMS, 1994, OCS Study MMS 94-0046; Gulf of Mexico Air Quality Study, Vol. 1 Summary of Data Analysis and Modeling). The VOC rates are based on measurements in 1993 and projected here to 1995 using production rates derived from API (2001). It should be noted that MMS estimates for VOC rates are based on only a two-month summer sampling program involving two platforms offshore Texas and Louisiana within the land-sea breeze corridor. Clearly this is a small data set with considerable uncertainty. Nevertheless the number seem to be consistent with the other sites in Tables 2-2 through 2-6.

VOC for Southern California (zone K) were calculated from numbers provided by the California Air Resources Board (CARB) inventory for 1997 in the Santa Barbara Channel (available on request from www.arb.ca.gov). Actual VOC in Table D-7 were calculated using the California VOC rate times the 1995 production from API (2001). These VOC rates are by far the most accurate estimates since they were based on detailed component (valves, internal combustion engines, etc.) counts multiplied by an assumed VOC emission rate per component (Tier 3 level).

The best estimate for Alaskan offshore platforms were based on the GOM VOC rates times the relevant 1995 production from API (2001). The best estimate of total VOC released in North America in 1995 is 60 kilotonnes/year with a lower bound of 36 kilotonnes/year and upper bound of 226 kilotonnes/year.

Worldwide Estimates

Table D-7 summarizes the worldwide estimates. It shows a best estimate of 649 kilotonnes per year with lower and upper bounds of 191 and 1,322 kilotonnes per year, respectively.

VOC rates for the U.K. sector were provided by U. K. Offshore Operators Association (http://www.ukoaa.co.uk). Estimates for the Norwegian Sector were provided by Norwegian Petroleum Directorate (Einang Gunnar). The estimates were combined and labeled "W. Europe."

No direct estimates of VOC data could be found for the remainder of the world so these were estimated by multiplying the VOC rate by the oil produced offshore in that region 1995 from API (2001a). One problem arose in doing this. The API (2001b) lumps Mexico with "Other Latin America." In order to estimate VOC for North America, the production volumes from Pemex (2000) were subtracted from the API "Other Latin America" and the resultant added to the API "Venezuela" estimate to get the value for "S. America shown in Table D-7.

OPERATIONAL (PRODUCED WATER) DISCHARGES INTRODUCTION

During oil production, water from the reservoir is also pumped to the surface. Under current industry practices, this "produced water" is treated to separate free oil and either injected back into the reservoir or discharged overboard. Produced water is the largest single wastewater stream in oil and gas production. The amount of produced water from a reservoir varies widely and increases over time as the reservoir is depleted. For example, in the North Sea, a maturing oil production area, the volume of produced water has increased at a rate of 10-25 percent per year over the period 1993-1997 in Norway (NOIA, 1998) and the United Kingdom (UKOOA, 1999). Norwegian oil fields produced about half as much water as oil (NOIA, 2000) in 1997. However, an increasing amount of the produced water is re-injected.

Produced water discharges are permitted as operational discharges. The oil and grease content is regulated by permit, and the allowable maximum concentrations vary by region and nation: For the U.S. Gulf of Mexico, the limit is 29 mg/L (USEPA, 1996); in the North Sea and Canada, it is 40 mg/L (PARCOM, 1986, PanCanada, 1999). Conventional treatment consists of oil/water separators, and there will have to be major technological advances before significant improvements in treatment efficiencies can be expected.

Tables D-8 and D-9 show the estimated volumes of water and oil discharges from offshore produced water discharges for North America and other major offshore producing regions, where available. Data from the 1985 Oil in the Sea report (based on 1979 offshore oil production volumes) are included for comparison. It should be noted that the 1979 estimates were calculated very indirectly; offshore oil production was multiplied by a water:oil ratio (which varied from 0.1 for the U.K. to 0.8 for the United States) and three concentrations for oil content (low, best estimate, and high) that varied by a factor of two. The 1979 estimate did not consider reinjection of produced waters.

PRODUCED WATER DISCHARGES IN NORTH AMERICA

The 1990s estimates were made using very different and more precise methods. In the United States and the North Sea, offshore operators are required to routinely monitor the volumes and oil content of produced water discharges and to submit reports to regulatory authorities to demonstrate compliance with discharge permits. Therefore, the 1990s estimates have a relatively high degree of certainty. For the United States, produced water discharge volumes and oil and grease content are reported in discharge monitoring reports (DMR) that are submitted monthly to the U.S. Environmental Protection Agency. Table D-8 includes detailed calculations for the different oil production areas in the United States and the North Sea.

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TABLE D-8 Estimates of Oil Discharges to the Marine Environment from Produced Water Discharges. NR = Not Reported

	Produced Water (1,000 bbl/yr)		Oil and Grease Content, in mg/L (min-max estimates)		Oil and Grease Discharge, in tonnes/yr (min-max estimates)	
Country	1979	1990s	1979[a]	1990s	1979[a]	1990s
Total U.S.A.[b]	311,300	745,000	50	20	2,228	2,500 (2,000-3,600)
Gulf of Mexico Offshore		473,000		20 (15-29)		1,700 (1,300-2,500)
Louisiana Territorial Seas		186,000		20 (15-29)		600 (450-860)
Texas Territorial Seas		4,300		~6.6		4.5
California Offshore		36,100		~18 (15-29)		85 (85-170)
Alaska Territorial Seas		45,700		15 (15-29)		110 (110-210)
Canada[c]	No offshore prod.	18,500	–	21 (15-29)	–	62 (32-85)
Mexico[d]	NR	15,200	NR	~60 (29-100)	NR	140 (70-230)
Total North America		780,000				2,700 (2,100-4,000)
U.K.[e]	57,400	1,620,000	60	25 (15-40)	486	5,700 (3,400-9,100)
Norway[f]	NR	450,000	NR	24 (15-40)	NR	2,000 (1,300-3,400)
The Netherlands[g]	NR	74,200	NR	NR (~35) (15-40)	NR	230 (100-260)
Denmark[h]	NR	NR	NR	NR	NR	160
Total North Sea						8,200 (5,000-13,000)
Other[i]	786,400				6,740	25,000 (12,000-41,000)
Totals					9,454	36,000 (19,000–58,000)

[a]Based on 1979 oil production volumes, water: oil ratios of 0.1 (U.K.) to 0.8 (U.S.A), and best estimate oil content of produced water.

[b]Data reported as means for various periods: Gulf of Mexico Outer Continental Shelf 1996-1998 (Rainey, pers. comm., 2000); Texas Territorial Seas Fourth Quarter 1999 (McClary, pers. comm., 2000); Louisiana Territorial Seas 1992 (Hale, pers. comm., 2000); California OSC 1989-1998 (Panzer, pers. comm., 2000); Alaska Territorial Seas 1997-1999.

[c]Data reported for 1999 only PanCanadian Petroleum Limited, 1999)

[d]Data reported for 1999 only (PEMEX, 2000)

[e]Data reported as means for 1996-1998 (UKOOA, 1999)

[f]Data reported as means for 1996-1997. Includes water and oil discharges for produced water and ballast/drainage water (NOIA, 1998)

[g]Data reported as means for 1995-1997 NOGEPA, 1998)

[h]Data reported for 1996 only NOGEPA (1998)

[i]See Table D-9.

TABLE D-9 Estimates of Oil and Grease Discharges from Produced Water Discharges in Other International Oil Production Areas, Using a Factor Derived from the Gulf of Mexico Offshore

Country	Oil Production Rate (kbbl/day)	% Offshore Production	Oil and Grease Discharge (tonnes/year)
Nigeria	2,000	80	6,000
Angola	750	100	2,800
Australia	600	100	2,300
Brazil	1,200	100	4,500
Venezuela	100	60	230
Indonesia	0	10	0
Malaysia	800	100	3,000
Thailand	130	50	250
China	320	10	120
India	235	10	90
Iran	200	5	40
Kuwait	280	18	190
Qatar	700	100	2,600
Saudi Arabia	2,000	25	1,900
United Arab Emirates	500	21	400
Totals			25,000

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For the Gulf of Mexico production facilities operating in the Outer Continental Shelf (OCS) region, MMS tracks the volume of produced water as part of their royalty program. MMS provided produced water volumes in barrels for 1996, 1997, and 1998, reported as a total of (1) injected on lease (i.e., injected back into a reservoir within the lease area), (2) injected off lease (i.e., injected into a reservoir outside the lease area, usually meaning that produced water is piped to another platform for re-injection), (3) transferred off lease (i.e., piped to a central facility for treatment and re-injection), and (4) overboard discharge (i.e., pumped into the water at the platform) (Gail Rainey, pers. comm., 2000). The overboard discharges were used as the volume of produced water discharged into marine waters for the offshore Gulf of Mexico. The DMR data for the Gulf of Mexico are not available in digital format, and the very large number of facilities makes it impossible to review each report to obtain specific data on the oil and grease content. Therefore, a default value of 29 mg/L, which is the maximum amount allowed for the Gulf of Mexico discharges, was used to estimate the maximum amount of oil and grease in offshore produced water discharges in the Gulf of Mexico. Industry operators attempt to keep oil and grease levels below 25 mg/L, so that the maximum will not be exceeded, and many operators are able to achieve levels below 20 mg/L (the long-term average for California was 18 mg/L and for Alaska was 15 mg/L). Thus, 20 mg/L represents the best estimate, and 15 mg/L was used to calculate the minimum estimate for this region. For the calculations, barrels of produced water were converted to liters, then multiplied by 20 mg/L to get mg of oil, that were then converted into tonnes of oil. Produced water discharged an estimated 2,000 tonnes per year of oil into offshore waters (Table D-8).

For the Gulf of Mexico production facilities in coastal waters, referred to as the territorial seas, there is no centralized tracking system. Texas Natural Resources and Railroad Commission (Kevin McClary, pers. comm., 2000) provided a summary of the quarterly reports of produced water volume (in bbls) and oil and grease content (in mg/L) for active dischargers for the fourth quarter of 1999. The volume of produced water discharges in Table D-8 was the total for this one period. The total oil and grease discharges were calculated by multiplying the volume by the oil and grease content for each discharge. For the 29 facilities that reported for this period, the average oil and grease content was calculated as 6.5 mg/L. The calculations were made as for the offshore discharges, that is, bbls of produced water converted to liters, multiplied by 6.5 mg/L to get mg of oil, that was converted to tonnes of oil. Produced water discharged an estimated 4.5 tonnes per year of oil into Texas coastal territorial waters (Table D-8).

For Louisiana territorial seas, the most recent summary of the more than 100 produced water discharges is for 1992, based on analysis of the DMRs. Louisiana Department of Environmental Quality (Doug Hale, pers. comm.) provided the estimate of 510,097 bbls per day of produced water discharges. There was no summary of oil and grease levels, so the best estimate default of 20 mg/L oil and grease was used. The calculations were made as for the offshore discharges, that is, bbls of produced water converted to liters, multiplied by 20 mg/L to get mg of oil, that was converted to tonnes of oil. Produced water discharged an estimated 600 tonnes per year of oil into Louisiana coastal territorial waters (Table D-8).

In California, all oil production occurs in the offshore. Fourteen platforms report produced water discharges (many platforms commingle their produced waters into one discharge point). MMS (Panzer, pers. comm., 2000) provided spreadsheets with the DMR data for the period 1989-1998 that had running means for produced water volume in barrels and oil and grease concentration in mg/L. The actual reported oil and grease concentrations and produced water volumes for each reporting period were used to calculate the total water volume and oil discharges for the region. The calculations were made as for the offshore discharges, that is, bbls of produced water converted to liters, multiplied by 18 mg/L to get mg of oil, that was converted to tonnes of oil Produced water discharged an estimated 85 tonnes per year of oil into federal offshore waters off California (Table D-8).

In Alaska, produced water discharges are reported for fourteen platforms, one tank farm, and one production facility, all discharging into Alaska territorial waters in Cook Inlet. The produced water volumes (in bbls) and oil and grease content, as reported on monthly DMRs for the period January, 1997, to December, 1999, were used to calculate annual averages for that period. For facilities that did not report an oil and grease concentration (e.g., the permit requires only a visual test for sheen), 15 mg/L, the average for all reporting facilities, was used. Produced water discharged an estimated 15 tonnes per year of oil into coastal territorial waters in Alaska (Table D-8).

Petroleos Mexicanos (PEMEX) published an annual report (PEMEX, 2000) describing its achievements in safety, health, and the environment. This report included a section on produced water discharges, stating that 79 percent of the 11.5 million cubic meters produced were reinjected, and reporting a total amount of oil discharged in tonnes. It was assumed that all of the produced water discharges were to marine waters. Using these data, the volume of produced water discharged to the sea in 1999 was calculated to be 15,190,000 bbls. The oil content of produced water (60 mg/L) was calculated by dividing the reported total oil discharges for produced water by this volume, so there is some uncertainty in this number.

Canada started offshore oil production in eastern Canada in 1996. Produced water volumes, oil levels, and total oil discharges in 1999 were reported in a 1999 discharge summary for the Cohasset Project published by PanCanadian Petroleum Limited. These data for 1999 are shown in Table D-8.

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INTERNATIONAL PRODUCED WATER DISCHARGES

In the North Sea, operators sample twice each day and prepare annual summaries that report the total produced water volumes, average oil content, and total amount of oil discharged to the sea. These reports are posted on web sites by the offshore operator associations for each country. The values in Table D-8 for the North Sea were derived directly from the available annual summaries, as described below.

The Netherlands Oil and Gas Exploration and Production Association reported annual oil discharges into Dutch waters in tonnes for 1987-1997 (NOGEPA, 1998). Table D-8 shows the average for the last three years, 1995-1997. NOGEPA (1998) also included a table listing oil discharges from produced water for Denmark for 1996.

The Norwegian Oil Industry Association published a summary of emissions to air and discharges to sea (NOIA, 1998) for the period 1990-1997. This report included total produced water volumes, amount reinjected, amount discharged to the sea, oil concentration, and total oil discharged in tonnes. The values for Norway in Table D-8 are means for the period 1996-1997, and include oil discharges from produced water and ballast and drainage water.

In the 1999 annual report by the United Kingdom Offshore Operators Association (UKOOA, 1999), produced water volumes, oil levels, and total oil quantity discharged in tonnes were provided for 1996-1998. These values are included in Table D-8.

For other international areas, where discharge summaries could not be obtained, a rough estimate was made, as follows. A "factor" was developed for the Gulf of Mexico offshore region, by dividing the oil discharge per year in tonnes by the oil production rate for this region. That is, the 1996-1998 maximum amount of 2,500 tonnes of oil from produced water discharges (representing an oil content of 29 mg/L in the produced waters, shown in Table D-8, was divided by the 1999 oil production rate of 1,354 kbbl/day, obtained from the U.S. Department of Energy (DOE, 1999), to get the minimum discharge amount. This approach avoids the need to convert from barrels to tonnes of oil. The U.S. Department of Energy provides data on the oil production rate for international regions. The percentage of production that is offshore is the same estimate used for estimating emissions for VOC. The best estimate was based on an oil and grease content of 60 mg/L, and the maximum estimate was calculated 100 mg/L. Based on this analysis, other international oil production areas discharge 25,000 tonnes of oil and grease per year.

The total amount of oil discharged with produced water discharged for the late 1990s is estimated to be 36,000 tonnes. This volume cannot be compared with the estimate made in 1979 because of the different methods used to make the two estimates. The 1990s volume is based on detailed monitoring and should be considered relatively certain.

One issue that could affect the uncertainty of the amount of oil discharged with produced water is the use of the standard Environmental Protection Agency (EPA) gravimetric method for determining oil and grease in the United States (EPA Method 413.1). A study of three Gulf of Mexico platforms found that 2-17 percent of the oil and grease was hydrocarbon material; the nonhydrocarbon components in the oil and grease analysis are fatty acids, phenols, and related compounds (Brown et al., 1992). For three California platforms, petroleum hydrocarbons comprised 30-60 percent of the total hydrocarbons in produced water (Schiff et al., 1992). In the North Sea, total oil is measured by infrared spectroscopy, which also includes nonpetroleum hydrocarbons. Therefore, the total oil discharges in Table D-8 are likely to be high, by as much as a factor of two to five.

There have been some major changes in permitted discharges for the oil and gas production industry during the 1990s that are not included in Tables D-8 and D-9. In the United States, produced water discharges into coastal waters (into estuarine areas landward of the shoreline) in the Gulf of Mexico were prohibited by the late 1990s (40 CFR 435.43). Annual produced water discharges into coastal waters in Louisiana in the early 1990s were estimated to be 222,832,000 bbls and contained 1,170 tonnes of oil and grease (Boesch and Rabalais, 1989). By 1997, in the North Sea, discharge of oil-based drilling muds had been prohibited by all countries. In the United Kingdom, oil discharges with drilling cuttings were 3,965 tonnes and represented 40 percent of the total oil releases to the North Sea by the United Kingdom.

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E

Inputs of Petroleum Hydrocarbons into the Oceans Due to Transportation Activities

Petroleum hydrocarbon inputs into the oceans from transportation activities are developed herein. Significant sources include operational discharges from ships, oil spills from tankers and non-tank vessels, operational discharges from recreational craft, and discharges from aircraft. Inputs due to atmospheric deposition of volatile organic compounds (VOC) vented from tankers are covered in Appendix H.

INPUTS TO THE SEA FROM MARITIME TRANSPORTATION

Operational Discharges in International Waters

Oil inputs into the sea from marine sources are naturally correlated to the number and types of vessels in operation in the marine environment. The number of tankers is significant because tankers are permitted discharges related to both cargo and propulsion machinery. The number of other ships is significant because they are permitted machinery related discharges. Table E-1 shows the comparison of the world's seagoing merchant fleet of ships not less than 100 GT for 1971, 1980, 1989, and 1999 (IMO, 1990 and Lloyd's Register, 1999).

The International Convention for Prevention of Pollution from Ships (MARPOL 73/78) regulates the design, construction, and operation of commercial vessels 100 gross tons (GT) and over worldwide with the goal of reducing or eliminating the discharge of oil and other pollutants into the sea. Many aspects of MARPOL (73/78) are of particular relevance during the calculations of estimates of input of petroleum hydrocarbon to the sea associated with marine transportation, including:

1. All commercial vessels between 100 and 400 gross tons are required to retain all oily waste on board, unless discharged at sea through special discharge control equipment as described below.
2. Tankers above 150 gross tons and all other commercial vessels over 400 gross tons are required to have installed oil/water separators (OWS) and oil discharge monitoring systems (ODMS), which continuously record the oil content of all overboard discharges from the bilges and, in the case of tankers, from any cargo slop tanks. For vessels above 10,000 gross tons, if oil content in the discharge stream is 15 parts per million (ppm) or greater, an alarm is supposed to sound and the discharge is terminated.
3. No tanker is permitted to discharge cargo oil effluent, even when using an ODMS, unless the vessel is underway between ports and more than 50 nautical miles from the nearest land. Therefore, for the purposes of this report all operational discharges of cargo oil are

TABLE E-1 Summary of the World's Merchant Fleet

	1971	1980	1989	1999
Number of Merchant Ships	55,014	73,832	76,100	86,817
Number of Tankers	6,292	7,112	6,383	7,270
Total Deadweight Tonnes (for Tankers)	169,354,743	339,801,719	247,556,000	298,731,000

NOTE: Non-propelled ships, ships of less than 100 gross tonnage, pleasure craft, naval auxiliaries, and ships restricted to harbor service or river/canal service are not included in the above.

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presumed to occur outside the waters of the United States or any other nation.

4. MARPOL has been adopted by nations with authority over 95 percent of the world's merchant vessels. In the United States, MARPOL has been adopted through the Act to Prevent Pollution from Ships (33 U.S. Code 1901 et seq.)
5. Discharges of bilge water and certain cargo tank washings from tankers are the only permitted discharges under MARPOL.
6. Discharge of fuel oil sludge is prohibited.
7. In order to assist vessels in complying with these prohibitions against discharge of excess quantities of oil and oil sludge into the water, waterfront facilities (where commercial vessels are received) are required to establish and maintain oil waste reception facilities. These oil waste reception facilities are suppose to have sufficient capacity to receive and process all oily wastes generated by all vessels calling at the facility.

Failure to have reception facility capability is supposed to result in vessels being denied entry to the facility. For example, International Maritime Organization's (IMO) 1998 list of waste reception facilities includes 1047 such facilities in various ports in the United States.

Operational Discharges from Cargo Tanks of Oil Tankers

Regulatory Background

During normal operations, certain tankers may discharge into the sea an amount of oil contained in the ballast and tank washings.

Under regulation 13 of MARPOL 73/78, tankers of 20,000 tonnes deadweight and above are required to have segregated ballast tanks (SBT), dedicated clean tanks (CBT), and/or crude oil washing systems (COW), depending on the vessel type, when they were built and their size. Regulation 13F adopted in 1992 restricts routing of ballast piping through cargo tanks and vice versa. These measures are designed to reduce operational and accidental pollution from tankers due to ballasting and tank washing.

Generally, crude oil carriers of 20,000 deadweight and above and product tankers of 30,000 tonnes deadweight and above delivered since 1983 must have SBT. Segregated ballast tanks are ballast tanks that are completely separated from the cargo oil and fuel oil systems, and which are permanently allocated to the carriage of water ballast. SBT greatly reduces the likelihood of oily ballast discharge, as there are sufficient segregated ballast tanks for normal operation in ballast. For these vessels, ballast may be allocated to cargo tanks only when needed to insure the safety of the vessel in particularly severe weather.

Unlike SBT, the piping systems for clean ballast tanks (CBT) may be common or connected with the cargo oil pump and piping systems. There are only a few CBT tankers operating today.

Crude oil washing is a system of cleaning cargo tanks using the dissolving action of crude oil to reduce clingage and sludge. Crude oil washing eliminates or reduces water washing, and thereby reduces operational oil pollution.

Regulation 9 of MARPOL limits the amount of oil that may be discharged into the sea to 1/15,000 of the total cargo oil volume for tankers built prior to the implementation of MARPOL73 (commonly referred to as Pre-MARPOL tankers), and 1/30,000 of the total cargo oil volume for MARPOL tankers. The requirement that the oil content of discharged effluent cannot exceed 15 ppm has the practical effect of limiting operational discharge to amounts much less than these maximum values.

Table E-2 gives the number and average deadweight for tankers in year 1999, and Table E-3 presents the age profile. More than two-thirds of the current fleet has SBT or double hull (DH) arrangements. MARPOL Regulation 13G requires mandatory retirement for single hull tankers at 30 years of age. A revision to regulation 13G currently under review will phase out all Pre-MARPOL tankers by 1 January 2007, at which time all MARPOL compliant tankers will have either SBT or DH arrangements.

SBT and Double Hull Crude Oil Carriers

According to industry sources (INTERTANKO, unpublished), SBT and double hull crude oil carriers will water wash 3-4 cargo tanks twice a year for inspection purposes. INTERTANKO estimates an average of 6,000 m^3 of wash water per tanker per year is discharged. Assuming an oil content of 15 ppm of oil, operational oil discharge is approximately 90 liters (0.08 tonnes) per year per tanker. Assuming 2/3 of the 1,782 crude oil carriers have SBT or DH arrangements, the total estimated discharge per year is as follows:

SBT and DH Crude Oil Carriers: 1,782•(2/3)•0.08 = 95 tonnes

For non-compliance vessels, where the ODMS is not working properly or intentionally bypassed, the estimated average discharge is 38 tonnes per year per tanker.

TABLE E-2 Summary of Number and Deadweight of Tankers for Year 1999 (Lloyd's Register, 1999)

	No. of Tankers	Deadweight (millions of tonnes)	Average Deadweight (tonnes)
Crude Oil Tanker	1,782	238.5	133,838
Product Tanker	5,269	43.5	8,256
Bulk dry/Oil Tanker	219	16.7	76,256
	7,270	298.7	41,087

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TABLE E-3 Age Profile of Tankers as a Function of Tonnes Deadweight (World Fleet Statistics, 1999)

	Crude Oil Carriers	Product Tankers	Dry Bulk / Oil Carriers	Total All Tankers
0–4 Years	22 percent	13 percent	7 percent	20 percent
5–9 Years	25 percent	11 percent	19 percent	22 percent
10–14 Years	11 percent	10 percent	21 percent	11 percent
15–19 Years	8 percent	21 percent	25 percent	11 percent
20–24 Years	28 percent	25 percent	24 percent	27 percent
25+ Years	6 percent	20 percent	14 percent	9 percent
Total	100 percent	100 percent	100 percent	100 percent

Pre-MARPOL Crude Oil Carriers

As discussed previously, these tankers carry ballast in their cargo tanks. Based on the Lloyd's Register (1999) statistics, the average deadweight of crude oil carriers is 133,844 tonnes. Assuming 30 percent of the deadweight is discharged as arrival ballast with an oil content of 15 ppm, the average quantity of water ballast per voyage is 40,153 tonnes and the average oil discharge is 588 liters or 0.528 tonnes. An industry survey undertaken by INTERTANKO indicates that 70 percent of all tankers carry a full load of cargo and 30 percent are partially loaded to an average of 60 percent of capacity. Consumables equaling about 5 percent of deadweight are also carried. Therefore, it is assumed that on the typical voyage a tanker carries cargo oil equal to approximately 80 percent of its deadweight. The average cargo oil moved on a crude oil carrier is 80 percent of 133,844 tonnes or about 107,075 tonnes, and the outflow factor, expressed as a fraction of the cargo oil moved, equals 0.0528 / 107,075 = 1 / 202,797. A rounded value of 1/200,000 is assumed for these calculations. This is a conservative estimate, as it assumes ballast is discharged at the maximum permissible oil content of 15 ppm, and also neglects the fact that many Pre-MARPOL tankers carry a portion of their ballast in segregated ballast tanks.

As reported by Concordia Maritime AB, an operator of a large fleet of Pre-MARPOL VLCCs (Very Large Crude Carriers), the average oil discharge from their Pre-MARPOL VLCCs is 300 liters per voyage. The average cargo volume for their VLCCs is approximately 300,000 m^3. Thus, the outflow factor attained by the Concordia fleet is (300/1,000) / 300,000 = 1 / 1,000,000. This is significantly better than the assumed factor of 1 / 200,000, but the performance level achieved by Concordia Maritime is believed to exceed standard practice.

For a crude oil washing system to be MARPOL certified, the oil found floating on top of the departure ballast after crude oil washing cannot exceed 0.00085 times the volume of the tanks containing ballast. On this basis, the oil content in the ballast tanks for this average size tanker is 33.3 tonnes. Assuming non-compliance where the ODMS is not working properly or intentionally bypassed, the oil outflow factor becomes 33.3 / 107,075 = 1 / 3,216. A rounded value of 1/3,000 is assumed for these calculations.

As summarized in Table E-4, the total outflow from non-SBT crude oil carriers is calculated as follows:

The crude oil carriers are divided into the following size ranges:
Less than 20,000 DWT
20,000 to 125,000 DWT (includes Panamax and Aframax tankers)
125,000 to 175,000 DWT (includes Suezmax tankers)
Greater than 175,000 DWT (includes VLCCs and ULCCs)

Within each size range, the number of crude oil carriers and the average deadweight are derived from 1999 statistics (Lloyd's Register, 1999). The number of voyages per annum for each size is estimated from industry sources (INTERTANKO, unpublished).

One-third of the crude oil carriers are assumed to regularly carry ballast in cargo oil tanks. Multiplying the number of tankers in each size range by 1/3 provides the estimated number of non-SBT tankers in 1999. Multiplying the average deadweight for each size by 80 percent provides the average quantity of cargo oil carried per voyage. The product of the number of non-SBT tankers, the quantity of cargo oil carried per voyage, and the number of voyages per annum provides the total cargo oil movement for each size range. Summing these figures gives the estimated cargo oil movements on non-SBT tankers of 1,000.8 million tonnes per year. Assuming an outflow factor of 1/200,000 as described above, the projected operational discharge in tonnes per year is as follows.

Non-SBT Crude Oil Carriers: 1,000,800,000/ 200,000 = 5,004 tonnes

Product Tankers

For 1999, the Lloyd's Register data show a total of 5,269 product tankers with an average deadweight of 8,256 tonnes. Their average cargo cubic is approximately 10,000 m^3. Assuming the volume of the slop tanks equals 3 percent of the

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TABLE E-4 Calculation of Operational Cargo Oil Discharge from pre-MARPOL (non-SBT) Crude Oil Carriers—Worldwide

	less than 20,000 DWT	20,000 to 125,000 DWT	125,000 to 175,000 DWT	greater than 175,000 DWT	all non-SBT Crude Tkrs
Total No. of Crude Oil Carriers	154	923	256	449	1,782
Assumed percent non-SBT	33.3 percent	33.3 percent	33.3 percent	33.3 percent	33.3 percent
No. of non-SBT Crude Oil Carriers	51	308	85	150	594
Average Deadweight (tonnes)	5,811	76,561	144,857	289,235	133,844
Cargo Oil as percent of Deadweight	80 percent	80 percent	80 percent	80 percent	—
Cargo Oil per Voyage (tonnes)	4,649	61,249	115,885	231,388	72,732
Voyages (per year)	40	30	15	8	23.2
Total Cargo Oil Moved (millions tonnes)	9.5	565.9	147.8	277.7	1,000.8
Discharge as percent of Cargo Oil Moved	1/200,000	1/200,000	1/200,000	1/200,000	1/200,000
Estimated Discharge (tonnes/year)	47	2,830	739	1,388	5,004

oil carrying capacity of the ship, the average slop tank capacity is 300 m^3. Assuming the slop tanks when charged with water have sufficient water for tank washing without introduction of additional water into the system, and that the full contents of the slop tanks are discharged at 15 ppm oil content, the projected operational oil discharge per voyage is about 4.5 liters. This corresponds to an outflow factor less than 1/2,000,000. Applying this factor for product tankers with SBT is a conservative assumption, as tank cleaning is not required in all circumstances, and cleaning is often carried out alongside a refinery where the slops can be transported ashore.

In the case of non-SBT product tankers where ballast is carried in cargo tanks, the outflow factor of 1/200,000 as applied for non-SBT crude oil carriers is appropriate. Annual discharges for non-SBT product tankers are developed similar to the crude carriers, and are summarized in Table E-5. The projected operational discharge in tonnes per year is as follows.

Non-SBT Product Tankers: 382,700,000 / 200,000 = 1,914 tonnes

Assuming 0.02 percent of the cargo oil remains onboard after offloading cargo, the average amount of oil remaining

TABLE E-5 Calculation of Operational Cargo Oil Discharge from pre-MARPOL (non-SBT) Product Tankers—Worldwide

	less than 20,000 DWT	20,000 to 125,000 DWT	all non-SBT Product Tkrs
Total No. of Product Tankers	4,545	724	5,269
Assumed percent non-SBT	33.3 percent	33.3 percent	33.3 percent
No. of non-SBT Product Tankers	1515	241	1756
Average Deadweight (tonnes)	2,894	41,911	8,255
Cargo Oil as percent of Deadweight	80 percent	80 percent	—
Cargo Oil per Voyage (tonnes)	2,315	33,529	5,643
Voyages (per annum)	40	30	38.6
Total Cargo Oil Moved (millions tonnes)	140.3	242.4	382.7
Discharge as percent of Cargo Oil Moved	1/200,000	1/200,000	1/200,000
Estimated Discharge (tonnes/year)	702	1,212	1,914

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onboard the product tankers is 2 m^3 or about 1.8 tonnes. For non-compliance where the ODMS is not working properly or intentionally bypassed, the oil outflow factor becomes 2 / 10,000 = 1 / 5,000.

This 1 / 5,000 factor is applied for both SBT and non-SBT product tankers. This is a conservative estimate, as it assumes that all oil remaining onboard the non-compliant tankers is discharged at sea. The oil discharge monitoring systems (ODMS) on clean product tankers have a higher degree of reliability as compared to vessels carrying persistent oils, and the discharge due to equipment failure should be less.

Summary of Operational Discharges of Cargo Oil from Tankers

Table E-6 summarizes total operational discharges assuming all tankers operate in compliance with MARPOL73/78. The estimated discharge per year is 7,396 tonnes.

In the 1990 study on inputs of petroleum into the marine environment (IMO 1990), the following estimates were made with regard to tankers complying with MARPOL maximum discharge quantities:

Greater than 150,000 DWT	99 percent compliance
75,000 to 150,000 DWT	95 percent compliance
40,000 to 75,000 DWT	85 percent compliance
20,000 to 40,000 DWT	85 percent compliance
Less than 20,000 DWT	80 percent compliance

The rationale for this degree of non-compliance is that 1) not all tankers fly the flag of a state that is party to MARPOL 73/78, 2) not all tankers that fly the flag of a state party to MARPOL 73/78 operate in compliance with the discharge criteria; 3) there will be equipment failures onboard ships, and, 4) there are not adequate reception facilities worldwide. The higher degree of compliance allocated to the larger tankers was justified on the basis that the large majority of the larger tankers fly the flag of a state party to MARPOL 73/78, and the majority of larger tankers are on longer voyages which facilitates compliance with MARPOL 73/78.

Since 1990, tanker operations have come under much closer scrutiny. Port state oversight has increased, and regulations such as the International Ship Management Code (ISM) and the Standards for Training and Certification of Watchkeepers (STCW) have encouraged more diligent operations. In view of the above, the assumed compliance rates have been increased to the following values.

Greater than 125,000 DWT	99 percent compliance
20,000 to 125,000 DWT	95 percent compliance
Less than 20,000 DWT	90 percent compliance

Table E-7 summarizes total operational discharges assuming these levels of compliance with MARPOL73/78. The estimated discharge per year is 36,437 tonnes (10,712,461 gallons). These discharges are applicable to international waters. Discharge of oily water within 50 nautical miles from shore is prohibited. Intentional discharges within U.S. and Canadian waters are believed to be small due to rigorous enforcement programs.

Bilge Oil and Fuel Oil Inputs

Machinery Space Bilge Discharges from Tankers

The large majority of commercial vessels above 100 GT in size are motor ships. The 1990 International Maritime Organization report estimated the average production of bilge oil at 12 gallons per day for a 20,000 HP plant. Advancements in the design and manufacture of engines and pumps, fitting of coamings around pumps and other sources of oil on new vessels, locating of the purifiers into separate spaces, and other design improvements have brought about a

TABLE E-6 Calculation of Operational Cargo Oil Discharge from Tankers Assuming Full Compliance with MARPOL 73/78

	Crude Oil Carriers DH or SBT	Crude Oil Carriers without SBT	Product Tankers DH or SBT	Product Tankers without SBT
No. of Tankers	1,188	594	3,513	1,756
Discharge per Tanker (tonnes per year)	0.08	—	—	—
Oil Movements (millions of tonnes/year)	—	1,000.8	765.5	382.7
Outflow Factor	—	1/200,000	1/2,000,000	1/200,000
Operational Discharge (tonnes/year)	95	5,004	383	1,914
Total Discharge (tonnes/year)	7,396			

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TABLE E-7 Calculation of Operational Cargo Oil Discharge from Tankers Assuming Partial Non-Compliance with MARPOL 73/78—Worldwide

	Crude Oil Carriers DH or SBT	Crude Oil Carriers without SBT	Product Tankers DH or SBT	Product Tankers without SBT
MARPOL Compliant				
No. of Tankers	1,140	570	3,187	1,593
Discharge per Tanker (tonnes per year)	0.08	—	—	—-
Oil Movements (millions tonnes/year)	—	965.1	713.3	356.7
Outflow Factor	—	1/200,000	1/2,000,000	1/200,000
Operational Discharge (tonnes/year)	91	4,825	357	1,783
Total discharge from compliant tkrs	7,056			
Non-compliant				
No. of Tankers	48	24	326	163
Discharge per Tanker (tonnes per year)	38	—	—	—-
Oil Movements (millions of tonnes/year)	—	35.8	52.1	26.1
Outflow Factor	—	1/3,000	1/5,000	1/5,000
Operational Discharge (tonnes/year)	1824	11,923	10,422	5,211
Total discharge from non-compliant tankers	29,381			
Total Discharge (tonnes/year)	36,437			
Total Discharge (gallons/year)	10,257,685			

reduction in bilge oil generation for modern ships. For these calculations, a rate of 5 gallons per day for a 20,000 HP plant, or 0.25 gallons per 1,000 HP per day is assumed.

An estimation of bilge oil generation for tankers is provided in Table E-8. The number of tankers is taken from the Lloyd's Register data for 1999, and the horsepower is estimated based on the distribution of tanker sizes. Assuming 0.25 gallons of bilge oil is generated per 1,000 HP per day, and that the tankers operate 350 days per year, it is estimated that a total of 19,119 tonnes (5.3 million gallons) of bilge oil is generated per year.

On crude oil tankers, oily bilge water is routinely transferred to the cargo slops system, which includes an oily water separator system where most of the oil is settled out and returned for use on the tanker. Periodically the water collected through this system must be discharged overboard through an oil discharge monitoring system set to alarm and shut down at 15 ppm. Product tankers are not able to recycle as much oil but, in any case, oil content of all overboard discharge is restricted to 15 ppm.

Assuming a 15 ppm oil content for bilge discharges, it is estimated that less than 0.2 percent of bilge oil is discharged overboard. Table E-9 summarizes the expected bilge oil discharge for tankers. The rate of MARPOL compliance is assumed as described in the previous section on operation discharges, and non-compliant vessels are assumed to discharge all of their bilge oil overboard. The discharge from MARPOL compliant tankers is very small—a total of only 34 tonnes per year. Total discharge from both compliant and non-compliant tankers is estimated at 1,129 tonnes (313,621 gallons) per year.

This is considered to provide a conservative estimate of legally permitted discharges. Steam tankers generate less oil to the bilges. Because steam tankers make up less than 5 percent of the world fleet, the above calculations assumed that all tankers are motorships.

Machinery Space Bilge Discharges from Non-Tankers

According to Lloyd's Register data there were 79,547 non-tankers above 100 GT in size operating commercially around the world in 1999. These consisted of 38,732 commercial vessels with an average main propulsion power of about 7,500 HP, and 40,815 other vessels with an average power of about 500 HP.

Bilge oil discharges for non-tankers are summarized in Table E-10. A bilge oil generation rate of 0.25 gallons/1000 HP per day was applied. Vessels between 100 GT and 400 GT, which comprise some 54 percent of the non-tanker fleet, are not required to have oily water discharge equipment installed. Although these vessels are not permitted to discharge bilge effluent, it is believed that there is a significant level of non-compliance. To account for this, 15 percent of the commercial vessels and 30 percent of the other vessels were assumed to not comply with MARPOL regulations.

Total bilge oil discharge from both compliant and non-compliant vessels other than tankers is estimated at 15,607 tonnes (4.0 million gallons) per year.

Fuel Oil Sludge from All Vessels

Based on 1998 data collected by INTERTANKO (unpublished), the world annual use of fuel oil from marine application is estimated to be 130 million tonnes of heavy residual fuel oil and 40 million tonnes of distillate fuel. Based on

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TABLE E-8 Generation of Bilge Oil for Tankers—Worldwide

	Crude Oil Carriers	Product Tankers	Dry Bulk/ Oil Carriers
No. of Tankers	1,782	5,269	219
Average Size of Propulsion Machinery (HP)	21,000	3,700	15,000
Assumed Bilge Oil Generation (gal/1000 HP/day)	0.250	0.250	0.250
Average Bilge Oil Generation (gal/day/ship)	5.3	0.9	3.8
Assumed Time in Service (Days/Year)	350	350	350
Bilge Oil Generation (gallons/year)	3,274,425	1,705,839	287,438
Bilge Oil Generation (tonnes/year)	12,038	6,059	1,021
Total Tankers Bilge Oil Generation (tonnes/year)	19,119		
Total Tankers Bilge Oil Generation (gallons/year)	5,267,701		

databases on marine bunker supply maintained by the Energy Information Administration (EIA) and the International Energy Agency (IEA), IMO estimated consumption during 1996 as 100 million tonnes of heavy residual fuel oil and 38 million tonnes of distillate fuel (IMO 2000). An unpublished study by INTERTANKO, which assessed consumption based on the world fleet makeup in year 2000 and the estimated consumption per vessel, estimated overall consumption at 224 million tonnes. For this report, the 1998 estimate of 170 million tonnes per year of fuel oil consumption is applied when calculating sludge generation.

Heavy fuel oils contain between 1 percent and 5 percent sludge or waste oil, which cannot be burned as fuel and therefore must be disposed of by other means. A value of 1.5 percent is applied for these calculations.

MARPOL prohibits the discharge of any of this sludge to the sea. Diesel fuel oil does not produce any appreciable quantity of sludge and therefore is discounted from further consideration here. The total production of sludge from ships is estimated as 130 million • 0.015 = 1.95 million tonnes (499 million gallons) of sludge per year.

As noted above, MARPOL requires that all sludge must either be retained on board for discharge to a reception facility ashore or for other legal treatment on board the vessel. On-board treatment includes mixing and homogenizing sludge with the fuel oil, use of on-board incinerators, and on crude oil tankers, transferring the sludge to the cargo or slop tanks.

Not all vessels are equipped with incinerators or slop tanks or have the capability to otherwise treat all produced sludge on board. Waste reception facilities exist throughout the world. There are over 1,000 such facilities in the United States alone. It is widely acknowledged that such facilities are not used to the fullest extent due to a variety of reasons

TABLE E-9 Bilge Oil Discharge from Tankers Greater Than 100 GT—Worldwide

	Crude Oil Carriers	Product Tankers	Dry Bulk/ Oil Carriers
MARPOL Compliant			
No. of Tankers	1,782	5,269	219
Total Bilge Oil Generation (tonnes/year)	12,038	6,059	1,021
Percent of Tankers Assumed MARPOL Compliant	96 percent	91 percent	93 percent
Discharge as a percent of Bilge Oil Generated	0.2 percent	0.2 percent	0.2 percent
Bilge Oil Discharge (tonnes/year)	23.2	11.0	1.9
Total discharge from compliant tankers (tonnes/year)	36		
Non-compliant			
Percent of Tankers Assumed Non-MARPOL Compliant	4 percent	9 percent	7 percent
Discharge as a percent of Bilge Oil Generated	100 percent	100 percent	100 percent
Bilge Oil Discharge (tonnes/year)	457.5	563.5	71.5
Total discharge from non-compliant tankers (tonnes/year)	1,092		
Total Discharge (tonnes/year)	1,129		
Total Discharge (gallons/year)	313,121		

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TABLE E-10 Bilge Oil Discharge from Non-Tankers Greater Than 100 GT—Worldwide

	Commercial Vessels	Other Vessels
Bilge Oil Generation		
No. of Ships	38,732	40,815
Average Size of Propulsion Machinery (HP)	7,500	500
Assumed Bilge Oil Generation (gal/1000 HP/day)	0.250	0.250
Average Bilge Oil Generation (gal/day/ship)	1.9	0.1
Assumed Time in Service (Days/Year)	350	100
Bilge Oil Generation (gallons/year)	25,417,875	510,188
Bilge Oil Generation (tonnes/year)	99,289	1,809
Marpol Compliant		
Percent of Vessels Assumed MARPOL Compliant	85 percent	70 percent
Discharge as a percent of Bilge Oil Generated	0.2 percent	0.2 percent
Bilge Oil Discharge (tonnes/year)	168.8	2.5
Total discharge from compliant ships (tonnes/year)	171	
Non-compliant		
Percent of Tankers Assumed Non-MARPOL Compliant	15 percent	30 percent
Discharge as a percent of Bilge Oil Generated	100 percent	100 percent
Bilge Oil Discharge (tonnes/year)	14,893	543
Total discharge from non-compliant tankers (tonnes/year)	15,436	
Total Discharge (tonnes/year)	15,607	
Total Discharge (gallons/year)	4,009,662	

including cost and timeliness. Therefore, it is generally assumed that some quantity of oily sludge is discharged to the sea in contravention of MARPOL. The previous study (IMO, 1990) estimated that quantity to be 10 percent for tankers and 25 percent for non-tankers. Recognizing improvements in vessel operations and enforcement regimes since then, for these calculations non-compliance is taken as 5 percent for tankers and 15 percent for non-tankers.

As shown in Table E-11, total sludge discharge to the sea from both compliant and non-compliant vessels is estimated at 255,700 tonnes (65 million gallons) per year.

Oily Ballast from Fuel Tanks

Discharges of oily ballast from fuel tanks are considered to be negligible. Placing seawater in fuel tanks as ballast water introduces contaminants into those tanks, increasing engine maintenance and the risk of malfunction. Thus, the practice is avoided whenever possible.

Summary of Bilge Oil and Fuel Oil Inputs

Bilge oil and fuel oil inputs are summarized in Table E-12. The total amount of oil entering the sea from these

TABLE E-11 Fuel Oil Sludge Discharge—Worldwide

	Tankers	Non-Tankers
No. of Ships	7,270	79,547
Average Size of Propulsion Machinery (HP)	8,281	3,908
Fuel Oil Consumption—Residual Fuel (million tonnes)	24.5	105.5
Fuel Oil Consumption—Distillate Fuel (million tonnes)	0.0	40.0
Sludge Content of Residual Fuel	1.5 percent	1.5 percent
Sludge Content of Distillate Fuel	0.0 percent	0.0 percent
Sludge Generation (tonnes/year)	368,004	1,581,996
Percent of Ships Assumed Non-MARPOL Compliant	5 percent	15 percent
Sludge Discharge (tonnes/year)	18,400	237,299
Total Sludge Discharge (tonnes/year)	255,700	
Total Sludge Discharge (gallons/year)	65,459,110	

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TABLE E-12 Total Amount of Oil Entering the Sea from Bilge and Fuel (1989 Figures from IMO, 1990)—Worldwide

	IMO 1989 (tonnes)	Year 1999 (tonnes)	Best Estimate (gallons)
Machinery Space Bilges	64,400	16,736	4,322,783
Fuel Oil Sludge	186,800	255,700	65,459,110
Oily Ballast From Fuel Tanks	1,400	0	0
Total	252,600	272,435	69,781,893

sources is estimated as 272,435 tonnes (70 million gallons). The discharge of sludge accounts for about 94 percent of the total bilge oil and fuel oil input.

Fuel Oil and Bilge Oil Inputs in North American Waters

Bilge oil discharges into U.S. marine waters for vessels greater than 100 GT in size are summarized in Table E-13. Intentional discharges of cargo oil washings and sludge within U.S. and Canadian waters are believed to be small due to rigorous regulatory enforcement programs, and are assumed to be included in the spill data.

Transit miles for tankers and cargo ships operating in U.S. waters are obtained from ACOE transit data (U.S. Army Corps of Engineers Navigation Data Center, 1997b). The number and average horsepower of commercial vessels other than tankers and cargo ships is obtained from the U.S. Coast Guard Marine Safety Management System (MSMS) database. These data are used to estimate operating days in U.S. coastal waters for these other vessels. Recreational vessels and government vessels were not considered in this estimate.

The quantity of bilge oil generated is calculated assuming 0.25 gallons of bilge oil is produced per 1,000 HP per day. For MARPOL compliant vessel, it is estimated that less than 0.2 percent of bilge oil is discharged overboard. For non-compliant vessels, 100% discharge of bilge oil is assumed.

Recognizing the strong port state control measures in effect in both the U.S. and Canada, for these calculations 98% compliance with MARPOL regulations is assumed for vessels greater than 400 GT. For smaller vessels, which are not required to have oil/water separators and therefore must transfer contaminated bilge water ashore, 90% compliance is assumed. Assuming these levels of compliance, the total estimated operational discharges of bilge oil into marine U.S. waters per year is 81 tonnes (22 thousand gallons)

Table E-14 summarizes total operation discharges in North American waters. The figures for Canada and Mexico were derived by multiplying the estimated operational discharge in U.S. waters by the ratio of cargo movements in U.S. waters to the cargo movements in Canadian and Mexican waters respectively. The best estimate of total discharge in North American waters is 99 tonnes (26 thousand gallons). Approximately 38 tonnes (11 thousand gallons) are diesel oil, with the remaining 61 tonnes (16 thousand gallons) comprised primarily of heavy fuel oil and lube oil.

The tonnes of cargo moved through each region were used as a basis for distributing the total operational discharge of

TABLE E-13 Bilge Oil Discharge—U.S. Marine Waters (for vessels greater than or equal to 100 GT)

	Tankers	Vessels > 400 GT in size Cargo Ships	Other	100 GT to 400 GT
Days operating in U.S. coastal waters (days/year)	67,000	209,000	110,000	235,000
Average Size of Propulsion Machinery (HP)	7,500	8,300	3,900	1,200
Assumed Bilge Oil Generation (gal/1000 HP/day)	0.250	0.250	0.250	0.250
Average Bilge Oil Generation (gal/day/ship)	1.9	2.1	1.0	0.3
Bilge Oil Generation (gallons/year)	125,625	433,675	107,250	70,500
Bilge Oil Generation (tonnes/year)	491	1,694	380	250
MARPOL COMPLIANT				
Total Bilge Oil Generation (tonnes/year)	491	1,694	380	250
Percent assumed MARPOL Compliant	98.0	98.0	98.0	90.0
Discharge as a Percent of Bilge Oil Generated	0.2	0.2	0.2	0.0
Bilge Oil Discharge (tonnes/year)	1.0	3.3	0.7	0.0
NON-COMPLIANT				
Percent of Tankers Assumed Non-MARPOL Compliant	2	2	2	10
Discharge as a Percent of Bilge Oil Generated	100	100	100	100
Bilge Oil Discharge (tonnes/year)	9.8	33.9	7.6	25.0
Total Bilge Oil Discharge (tonnes/year)	81			
Total Bilge Oil Discharge (gallons/year)	21,687			

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TABLE E-14 Total Bilge Oil Discharge—North American Waters (for vessels greater than or equal to 100 GT)

	(tonnes)	(gallons)
United States	81	
Canada	11	
Mexico	7	
Best estimate	99	26,465

bilge oil amongst the various zones. These results are summarized in Table E-15.

Summary of Fuel Oil and Bilge Oil Inputs (for Vessels greater than or equal to 100 GT)

Estimated operational discharges for both North American waters and international waters are summarized in Tables 2-2 through 2-6. Considering the high level of uncertainty in the assumptions on the extent of MARPOL compliance, the minimum estimate is taken as 50% of the best estimate, and the maximum estimate at twice the best estimate.

Fuel Oil and Bilge Oil Inputs in North American Waters (for Vessels less than 100 GT)

Bilge oil discharges into U.S. marine waters for vessels less than 100 GT in size are summarized in Table E-16. According to U.S. Coast Guard Marine Safety Management System (MSMS) database, in year 2000 there were 41,313 registered vessels in the U.S. under 100 GT, other than tankers, cargo ships, and recreational vessels. This average size for propulsion machinery was 350 HP. It was assumed that these vessels generated 0.09 gallons of bilge oil per day, operated 50 days per year, and that 60% of the vessels operated in marine (non inland) waters. These estimates were the best judgment of the committee, as data were not available. Based on the above, the total bilge oil generation in the vessels less than 100 GT was calculated to be 385 tonnes per year (108 thousand gallons per year).

A 70% compliance level was assumed for these smaller vessels. For MARPOL compliant vessels, it is assumed that all bilge oil is retained onboard and disposed at suitable reception facilities. For non-compliant vessels, 100% discharge of bilge oil is assumed. The calculated value, also considered the best estimated, was therefore 30% of 385 tonnes per year, or 115 tonnes per year (33 thousand gallons per year). All of these discharges are assumed to be diesel oil and other light distillates. The distributions by zone are summarized in Table E-18. Due to the very high level of uncertainty in these calculations, a range from 23 tonnes per year (20% of the best estimate) to 575 tonnes per year (five times the best estimate) was selected. Worldwide estimates for vessels under 100 GT were not developed due to the lack of data. Also, estimates were not developed for Canadian and Mexican waters.

Accidental Spills from Vessels in North American Waters

Spill Trends in U.S. Waters

Figure E-1 shows the oil spillage in U.S. waters from tank vessels during the period from 1973 to 1999. The oil spill data are from the Environmental Research Consulting Spill

TABLE E-15 Operational Discharge Summary (for vessels greater than or equal to 100 GT)

	Best Estimate (tonnes)	Minimum (tonnes)	Maximum (tonnes)	Best Estimate (gallons)	Minimum (gallons)	Maximum (gallons)
North American Waters						
Machinery Space Bilges	99			26,465		
Fuel Oil Sludge	0			0		
Oily Ballast From Fuel Tanks	0			0		
Total—North American Waters	99	33	300	26,000	9,000	80,000
International Waters						
Machinery Space Bilges	16,637			0		
Fuel Oil Sludge	255,700			0		
Oily Ballast From Fuel Tanks	0			0		
Total—International Waters	270,000	90,000	810,000	70,000,000	23,000,000	210,000,000
Worldwide						
Machinery Space Bilges	16,736			4,322,783		
Fuel Oil Sludge	255,700			65,459,110		
Oily Ballast From Fuel Tanks	0	0				
TOTAL—WORLDWIDE	270,000	90,000	810,000	70,000,000	23,000,000	210,000,000

NOTE: All totals rounded to two significant figures.

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TABLE E-16 Total Bilge Oil Discharge—North American Waters (for vessels less than 100 GT)

Number of Registered Vessels < 100 GT in size	41,313
Estimated percentage operating in marine waters	60
Estimated operating days per year	50
Days operating in U.S. coastal waters (days/year)	1,240,000
Days operating in U.S. coastal waters (days/year)	1,240,000
Average Size of Propulsion Machinery (HP)	350
Assumed Bilge Oil Generation (gal/1000 HP/day)	0.250
Average Bilge Oil Generation (gal/day/ship)	0.088
Bilge Oil Generation (gallons/year)	108,500
Bilge Oil Generation (tonnes/year)	385
MARPOL Compliant	
Total Bilge Oil Generation (tonnes/year)	385
Percent assumed MARPOL Compliant	70
Discharge as a Percent of Bilge Oil Generated	0.0
Bilge Oil Discharge (tonnes/year)	0.0
Non-compliant	
Percent of Tankers Assumed Non-MARPOL Compliant	30
Discharge as a Percent of Bilge Oil Generated	100
Bilge Oil Discharge (tonnes/year)	115.4
Total Bilge Oil Discharge (tonnes/year)	115
Total Bilge Oil Discharge (gallons/year)	32,885

Databases, which collate data from a number of sources, including the U.S. Coast Guard, U.S. National Response Center, the U.S. Minerals Management Service, and the *Oil Spill Intelligence Report*.

As illustrated in Figure E-1, oil spillage dropped off significantly after 1991. This improvement followed the grounding of the *Exxon Valdez* in 1989, and the subsequent passage of the Oil Pollution Act of 1990 (OPA 90).

Estimated Spill Rates for North American Waters

In recognition of the fundamental changes to the maritime industry that took place after the *Exxon Valdez* accident, spill data from 1990 onward were used as the basis for estimating the amount of oil entering U.S. waters from marine vessel accidents. Because complete spill data for Canadian and Mexican waters are not available, the estimated input from these waters was based on U.S. spill data adjusted for the relative tonnage moved through Canadian and Mexican waters as compared to U.S. waters.

Although effort is required to carefully evaluate data from the U.S. Coast Guard spill database to avoid double counting, the data were consistently collected during the 1990s and are considered reliable, particularly with regard to the larger spills. The database, which contains generally conservative estimates of outflow from all reported incidents, is assumed to establish the minimum estimate.

Table E-17 lists the amount of petroleum hydrocarbons spilled in the sea in U.S. marine waters from 1990 through 1999. A total of 1,745 spills of 0.34 tonnes (100 gallons) or more occurred during this ten year period, discharging some 9,111 tonnes (2,520,134 gallons) into marine waters. 175 of these spills were greater than 34 tonnes (10,000 gallons) in size, and these large spills accounted for about 87% of the total spillage.

Table E-18 shows the breakdown of the spillage by types of vessels and types of oil. Tankers and tank barges were responsible for 82% of the total spillage. Oil types were separated into four categories. Spillage by oil type was as follows: crude Oil (36%), heavy distillate (36%), light distillate (25%), and gasoline (3%).

Estimation of Spills in Canadian and Mexican Waters

Because a comprehensive spill database for Canadian and Mexican waters were not available, the spill volumes were estimated by adjusted U.S. figures by the relative movements of cargo. In 1997, approximately 715 million tonnes of crude oil and products were moved in U.S. international and coastwise trade (USACE, 1997b). In comparison, about 68 million tonnes were moved through Canadian ports (Statistics Canada, 1997), or 9.5 percent of the U.S. movements. Similarly, about 112 million tonnes of crude and products were moved through Mexican ports (BP World Statistics, 1997), or 15.7 percent of the U.S. movements. Inputs from accidental spills from tank vessels in Canada and Mexico were taken as 9.5 percent and 15.7 percent of the U.S. values respectively.

Canadian and Mexican dry cargo movements are approximately one-third and one-twentieth of the U.S. international and coastwise movements respectively. However, freighters are responsible for only 18 percent of the spillage from other vessels in U.S. waters. It was assumed that spills in Canadian water from other vessels equals 15 percent of the U.S. totals, and that spills in Mexican waters from other vessels equals 6 percent of the U.S. totals.

Summary of Spills in North American Waters

The U.S. Coast Guard database, which contains generally conservative estimates of outflow from all reported incidents, is assumed to establish the minimum estimate. Recognizing the completeness of the data, the spill quantities were increased by just 5 percent to obtain the best estimate, and further increased by 20 percent to obtain the maximum estimate. Results are summarized in Table E-19.

The recording of the location of spills was not as consistently maintained within the U.S. Coast Guard spill database. This data has been reviewed and summarized in Tables 2-2 through 2-6, in order to provide a sense of the distribution of spills within U.S. waters.

Accidental Spills from Vessels in International Waters

For this study, spill data from the Environmental Research Consulting database is applied. This database includes information gleaned from the International Maritime Organization, ITOPF, and other national and regional agencies. The international data excludes spills in North American waters. As shown in Table E-20, a total of 745,292 tonnes of oil spillage was recorded during the years 1990 through 1999,

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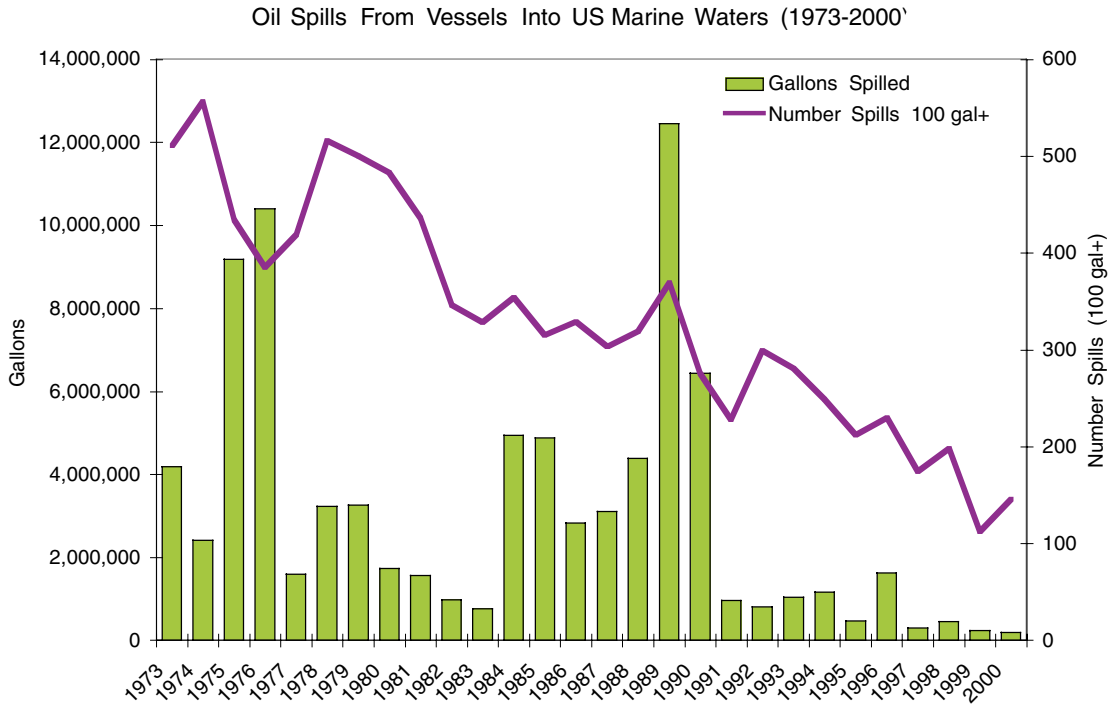

FIGURE E-1 Historical trend (1973-1999) in oil spills from vessels into U.S. marine waters (data from U.S. Coast Guard and MMS databases by Environmental Research Consulting.)

averaging 74,529 tonnes (22 million gallons) per year during this ten year period. Not included in these totals is the spillage associated with the Gulf War, which is estimated to be in excess of 600,000 tonnes.

The international data are not consistently collected and are therefore regarded as underestimates. Smaller spills are frequently not included, and reporting is sometimes compromised for political and logistical reasons. Recognizing the

TABLE E-17 Summary of Oil Input from Accidental Spills (for Vessels in U.S. Waters)

	Tanker			Tank Barge			Other Vessels		
Year	# Spills >100 gal	Amount Spilled (gallons)	Amount Spilled (tonnes)	# Spills >100 gal	Amount Spilled (gallons)	Amount Spilled (tonnes)	# Spills >100 gal	Amount Spilled (gallons)	Amount Spilled (tonnes)
1990	24	4,605,092	16,963	58	1,389,000	5,061	193	437,584	1,589
1991	13	43,348	154	39	631,934	2,431	176	279,274	1,020
1992	22	114,431	422	41	342,823	1,319	236	319,337	1,131
1993	26	78,729	300	42	661,848	2,562	213	301,703	1,111
1994	17	62,502	237	46	900,841	3,442	186	191,300	679
1995	10	84,369	304	33	70,492	251	169	304,268	1,110
1996	11	275,223	1,032	40	1,116,606	3,983	179	226,322	819
1997	5	3,952	15	27	139,447	482	142	145,493	531
1998	9	39,330	153	27	169,490	622	162	247,736	875
1999	4	4,590	17	19	157,680	511	89	67,117	246
Totals	141	5,311,566	19,597	372	5,580,161	20,665	1745	2,520,134	9,111
Ave./yr	14	531,157	1,960	37	558,016	2,067	175	252,013	911

Total—All Vessels—U.S. Waters (average over period from 1990-1999)

Number of Spills	226	spills > 100 gallons in size per year
Amount of Spillage	1,341,186	gallons spilled per year (average)
	4,937	tonnes spilled per year (average)

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TABLE E-18 Summary of Average Total Load from Accidental Spills during Years 1990-1999, for Vessels in U.S. Waters by Type of Vessel and by Type of Oil (tonnes)

	Tankers	Tank Barges	Other Vessels	Totals	% of Total
Crude oil	16,525	1,184	162	17,872	36%
Gasoline	187	1,459	50	1,697	3%
Light distillate	545	5,466	6,247	12,259	25%
Heavy distillate	2,340	12,556	2,651	17,546	36%
TOTALS	19,597	20,665	9,110	49,373	
(Percent of total)	40	42	18		

incompleteness of the data and the fact that the smaller spills, under 10,000 gallons (34 tonnes), comprised about 13 percent of the U.S. totals, the international spill quantities were increased by 25 percent to obtain the minimum estimate, by an additional 10 percent to obtain the best estimate, and further increased by 25 percent to obtain the maximum estimate. Results are summarized in Table E-21.

Accidental Spills from Vessels Worldwide

The North American and international spill estimates are combined to provide worldwide estimates (Tables 2-2 through 2-6). The best estimate for total spillage worldwide is 110,000 tonnes (30 million gallons) per year. The 1985 report (National Research Council, 1985) and the 1990 study (IMO, 1990) both used data from the International Tanker Owners Pollution Federation Ltd. (ITOPF) to estimate the quantity of oil entering the marine environment from tanker accidents. In the 1990 study, the spillage was averaged for the 10-year period from 1981 to 1989, establishing an annual average of 114,000 tonnes per year. In the 1990 report no adjustments were made for the deficiencies in the database, so care should taken when comparing these figures.

Inputs To The Sea From The Aircraft Industry

There are inputs to the sea from deliberate and continual releases of fuel from aircraft. There are two sources: deliberate discharge due to emergency conditions aboard the aircraft, and normal operation releases including the release of partially burned fuel in inefficient engines or inefficient operating modes and emptying of fuel injection bypass canisters. Modern aircraft have take-off weights exceeding their landing weights, sometimes by as much as 150 tonnes. For example, a 747 can carry as much as 220,000 L of fuel weighing about 175,000 kg or 175 tonnes. If a fully laden 747 jettisoned its fuel because it was required to return to an airport, it could dump as much as 150 tonnes of the fuel to enable it to land safely. Fuel dumping is infrequent but not rare. One airport reported on 16 fuel dumps in one year out of 7,000 flights conducted [Canadian Environmental Assess-

TABLE E-19 Summary of Average Annual Loads from Accidental Spills (for Vessels in North American Waters)

	Tank Vessels (gallons)	Other Vessels (gallons)	All Vessels (gallons)	Tank Vessels (tonnes)	Other Vessels (tonnes)	All Vessels (tonnes)
Spill Volume—U.S. Waters (per year)	1,089,173	252,013	1,341,186	4,026	911	4,937
Est. Spill Volume—Canada (per year)	100,000	38,000	138,000	384	137	521
Est. Spill Volume—Mexico (per year)	170,000	15,000	185,000	631	55	686
	1,359,173	305,013	1,664,186	5,042	1,102	6,144

	Tank Vessels		Other Vessels	
	(gallons)	(tonnes)	(gallons)	(tonnes)
North American Waters				
Minimum (based on 1990's data)	1,400,000	5,000	300,000	1,100
Best Estimate (1990's data + 5 percent)	1,400,000	5,300	300,000	1,200
Maximum (Best estimate + 20 percent)	1,700,000	6,400	400,000	1,400

NOTE: All totals rounded to two significant figures.

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TABLE E-20 Summary of Oil Input from Accidental Spills for Vessels (International Waters—Spills in North American Waters Excluded)

Year	Tank Vessels Amount Spilled (tonnes)	Other Vessels Amount Spilled (tonnes)	All Vessels Amount Spilled (tonnes)
1990	39,687	4,757	44,444
1991	169,077	4,315	173,393
1992	113,171	2,454	115,624
1993	107,895	3,269	111,164
1994	96,652	6,220	102,872
1995	12,439	4,358	16,797
1996	62,507	7,358	69,864
1997	62,846	3,344	66,190
1998	20,516	3,839	24,355
1999	17,613	2,976	20,589
Totals	702,402	42,890	745,292
Ave./yr	70,240	4,289	74,529

Total—All Vessels—International Waters
(average over period from 1990-1999)
Amount of Spillage 21,911,596 gallons spilled per year (average)
74,529 tonnes spilled per year (average)

ment Agency (CEAA), 1995]. The U.S. military reports on 938 dumps, for 7,300 tonnes per year, worldwide (Clewell, 1980). Reporting on dumping is required but is not enforced or monitored. Because of fears of dumping over residential areas, most dumping is conducted over preassigned areas of little habitation. Airports near lakes or oceans designate areas over these waters. Evaporation reduces the amount that directly deposits to between 5 and 70 percent of dump volume, depending on fuel type and weather conditions.

Older engines can emit relatively large amounts of unburned fuel. In older jet and turbine engines, jet fuel is cycled through engine parts as a coolant and is then passed into the injection system. Because this flow must be maintained at certain levels, about 5 to 15 percent of fuel consumption can be emitted through the engines without fuel combustion. This loss occurs primarily during idle and take-off conditions and is least during cruise conditions. Little documentation on this has been found, and it may not contribute much oil to the sea. Some older engines also have an injection bypass tank that is emptied automatically after take-off. This is believed to be restricted to very few aircraft at this time.

The preliminary estimate of oil reaching the sea is based on the probability of a dump occurring. From literature, the rate of military jettisoning varies between 0.001 and 0.002 dumps per flight (Clewell, 1980a,b; CEAA, 1995); this averages 0.0015. If civilian rates were one-third of this, then the rate for civilian aircraft would be about 0.0005, or 5 flights out of 10,000. The flights over the oceans are relatively well known (European Commission, 1996). Flights over the North Atlantic average about 700 daily, over the North Pacific about 100 (not counting those over land on polar routes), and those over the southern hemisphere, are estimated at about 200 per day. This is 1,000 flights per day, with most flights consisting of large, wide-bodied aircraft such as the 757, 767, MD-11, and similar aircraft. The dumping of fuel typically releases 50 tonnes (50,000 L), of which about 50 percent would reach the sea surface, based on experimental deposition studies (Clewell, 1980a; Cross and Picknett, 1973). This would yield 4,500 tonnes per year. The U.S. military averaged 7,262 tonnes per year in 1975 to 1978, with a steady decrease. If we place this value at 4,000 tonnes currently and presume that only one-quarter of this was over water and would hit the water, then about 1,000 tonnes per year is the U.S. military

TABLE E-21 Summary of Oil Input from Accidental Spills for Vessels Worldwide

	Best Estimate (tonnes)	Best Minimum (tonnes)	Maximum (tonnes)	Estimate (gallons)	Minimum (gallons)	Maximum (gallons)
NORTH AMERICAN WATERS						
Tank Vessels	5,300	5,000	6,400	1,400,000	1,400,000	1,700,000
Other Vessels	1,200	1,100	1,400	300,000	300,000	400,000
Total—North American Waters	6,500	6,100	7,700	1,700,000	1,700,000	2,100,000
INTERNATIONAL WATERS						
Tank Vessels	96,580	87,800	120,725	28,394,621	25,813,292	35,493,276
Other Vessels	5,897	5,361	7,372	1,733,823	1,576,203	2,167,279
Total—International Waters	100,000	93,000	130,000	30,000,000	27,000,000	38,000,000
WORLDWIDE						
Tank Vessels	100,000	93,000	130,000	30,000,000	27,000,000	37,000,000
Other Vessels	7,100	6,500	8,800	2,000,000	1,900,000	2,600,000
Total—Worldwide	110,000	100,000	140,000	32,000,000	29,000,000	40,000,000

NOTE: All totals rounded to two significant figures.

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input. If the world input from military aircraft is triple this amount, then the world input is 3,000 tonnes. The sum total of aircraft dumping input is then estimated at 7,500 tonnes. It is estimated that 1/5 of these releases would take place over North American territorial waters on the basis of air traffic loading to and from North America, compared to the rest of the world. This again is subdivided by the approximate numbers of trans-ocean flights arriving/departing from airports in the designated regions (Tables 2-2 through 2-6).

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F

Inputs into the Sea from Recreational Marine Vessels

The 1985 NRC report *Oil in the Sea* did not discuss petroleum hydrocarbon inputs from operation of two-stroke engines used in outboard motors and personal watercraft (PWC) (also know as jet skis). In 1990, heightened awareness about the large number and the design inefficiencies of these engines led the US EPA to begin regulating the "nonroad engine" population under the authority of the Clean Air Act. Engines that fell under this category include lawn mowers, grass trimmers, chain saws, etc., as well as outboard engines for boats. In the 1990 EPA regulations, there was only preliminary data on hydrocarbon inputs into surface water from two-stroke engines. Since 1990, studies have provided better quantification of the inputs of hydrocarbons and gas additives such as MBTE into the air and water from two- and four-stroke engines (Juttner et al., 1995; Barton and Fearn, 1997; M. S. Dale et al., 2000; Gabele and Pyle, 2000). For this report, oil and gasoline inputs to the sea are calculated for two-stroke engines ranging in size from 16-175 horsepower (20-230 kW) that are fueled by a mixture of oil and gasoline. Four-stroke engines discharge approximately 10 times less fuel that two-stroke engines, and were not included in the calculation because the population of four-stroke outboard engines is not known. Discharge rates of fuel for diesel outboard engine and from inboard engines are not well characterized and were also not included in the calculation.

DESIGN FEATURES OF TWO- AND FOUR-STROKE ENGINES

Both two- and four-stroke engines create mechanical energy (movement of a crankshaft) from the combustion of fuel in a confined space (cylinder). The names reveal the number of piston strokes required to complete one power or combustion cycle.

There are two strokes in the combustion cycle common to both engine types: a compression stroke and a power stroke. In two-stroke engines, the combustion cycle is completed in two-stroke pistons and a single revolution of the crankshaft. Power is generated with each revolution of the crankshaft. The following description starts with the piston at the bottom of the cylinder:

1. As the piston travels upwards to the top of the cylinder, it compresses the gases inside the cylinder as well as closes off the transfer and exhaust parts. This is considered the compression stroke. At the same time, the motion of the piston causes a vacuum in the crankcase and air is drawn into the engine for the next cycle.
2. Ignition occurs when the piston is near the top of its travel, causing the fuel and air to expand and force the piston downward. This is the power stroke. As the piston travels downward, the exhaust travels the exhaust port is opened and the hot expanding gasses leave the cylinder. At the same time, the fresh charge in the crankcase is pressurized. As the piston moves farther down, the transfer port is opened and the fresh charge enters the cylinder. Any remaining exhaust gasses are pushed out of the exhaust port.

There is no pump or oil circulation system in a two-stroke engine, so oil is added to the gasoline to lubricate the moving parts in the engine. There is no extra valve mechanism to operate, as the piston acts as the valve, opening and closing the necessary ports. These features make these engines powerful and lightweight and therefore very popular as outboard engines on small boats.

Fuel and fuel additives that are not combusted can enter the surface water directly with the exhaust gasses through the exhaust port. Depending on how the fuel is introduced to the combustion chamber, two-strokes may emit unburned fuel and fuel additives. Before 1998, conventional two-stroke engines used either carburetors or injectors to mix fuel with air as it entered the crankcase. Since 1998, marine outboard

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manufacturers have been producing new, direct injected (DI) two-strokes, and the technology is still in its infancy. While there are various techniques used in DI, they all inject the fuel directly to the cylinder after or nearly after the exhaust ports close. Direct injected two-stroke engines generally have 80 percent less hydrocarbon emissions than their predecessors. In DI two-strokes, oil is introduced directly to the crankcase to lubricate the moving parts and not mixed with the fuel.

As the name implies, four-stroke engines use four piston strokes for each combustion cycle.

Data Sources and Assumptions

Data on boating activity including number of two-stroke engines, average hours of use for each boating type (gasoline outboard and personal watercraft) and average horsepower was collected from the EPA Nonroad Emission Model (Jansen and Sklar, 1998). Several recent reports have measured discharge rates for fuel such as BTEX or fuel additives (e.g. MBTE) into surface water by recreational boating (Juttner et al., 1995; Barton and Fearn, 1997; Dale et al., 2000, Gabele and Pyle, 2000). In this calculation, BTEX was used as a surrogate for gasoline with aqueous discharge rates ranging from 0.20 to 0.70 g kW^{-1} hr^{-1} (Gabele and Pyle 2000). It is well established that comparable size four-stroke engines and direct injection two-stroke engines discharge approximately 5-10 times less fuel than standard two-stroke engines (Gabele and Pyle [2000] and earlier references). To our knowledge there is no population data on the four-stroke engine population and the existing two-stroke population data does not differentiate between standard and DI engine types. Therefore we assume that all the two-stroke populations are standard models requiring fuel and gas mixtures (Tables 2-2 through 2-6).

The average hours of use nationwide for two-stroke PWC engines is 77.3 hours per year and for outboard engines is 34.8 hours per year and calculated from a model (US EPA (in preparation)). These values are lower than past values for average boating-use of 91 and approximately 150 hours/yr (US EPA 1991). (The former of these 1991 estimates was provided by the National Marine Manufacturers Association and based on boater surveys; the latter is from an earlier EPA model). The average hours of use in this study does not distinguish between seasonal differences between regions where boating use may vary considerably. For example, states in northern latitudes generally have a shorter boating season and it is limited to the summer season.

The EPA population model also does not distinguish between engines used in coastal waters and those used in inland lakes and rivers that may or may not connect to the coast. For these calculations, we assumed that between 20-80 percent (average 50 percent) of the petroleum hydrocarbon discharge from two-stroke engines was to fresh water such as lakes and rivers that either did not connect to the coastal water or was included in Section F on petroleum hydrocarbon inputs from nonpoint sources.

Results

Based on the discussion above, estimates for load of petroleum hydrocarbons to the ten U.S. coastal zones (see Tables 2-2 through 2-6) were calculated as follows.

Sample Calculation

$$engine \times hp \times \frac{hrs}{engine\ year} \times \frac{g}{kW\ hrs} \times \frac{kW}{hp} \times \frac{l}{g} \times \frac{gallons}{l} = \frac{gallons}{year}\ fuel$$

Where:

Engine is the two- stroke standard engine population is from the boater registrations for each coastal county from the EPA population model.

Horsepower for two-stroke personal watercraft followed the EPA population model and divided into 4 categories (≤ 18.5, 35.4, 44.4, 75.1, 111) and 10 categories for outboard engine population (≤ 2.4, 5.2, 8.7, 15, 21.6, 35.7, 48.5, 78.3, 139, 228).

Hours of engine use per year is 77.3 hour $year^{-1}$ for PWC and 34.8 hours $year^{-1}$ for outboard engines for the entire United States (US EPA in preparation)

Discharge rate for BTEX is 0.21 g kW^{-1} $hour^{-1}$ (Benzene), 0.70 (Toluene), 0.2 (Ethylbenzene), 0.55 (Xylene) (Gambel and Pyle 2000).

Conversion factor I 0.75 kW/ $horsepower^{-1}$.

Density of hydrocarbon (gasoline) is 739.966 g L^{-1}

Conversion factor II 3.79 l/$gallon^{-1}$

ADDITIONAL CAVEATS

BTEX is 37.4% of gasoline (Saeed and Al-Mutairi 1999)

Assumption: the amount of fuel that enters the marine environment is estimated at 50% (range 20-80 %)

Oil mixture is 2 % of the fuel mixture in two-stroke engines.

Final fuel inputs were reduced by 45% to account for the decrease in fuel emission with increased engine size. (www.epa.gov/otaq/certdata.htm).

Overall, oil and gas inputs from two-stroke outboard motors are estimated to be between 0.6 to 2.5 million gallons per year (average 1.6 million gallons) or between 2,100 and 8,500 tonnes (average 5,300 tonnes) per year for coastal waters of the United States.

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G

Spills from Coastal Facilities

For this discussion facilities are defined as point sources of spills that are not vessels or oil and gas exploration and production facilities (including crude oil pipelines). Table G-1 lists the types of facilities included in this discussion. The U.S. Coast Guard database of spills greater than 100 gallons for 1990-1999 was used to estimate the amount of oil spilled from facilities (see detailed discussion of spill data used, available at http://www4.nationalacademies.org/dels/annex.nsf). The U.S. Coast Guard defines a facility as a spill source that is not a vessel; therefore the database had to be analyzed to remove spills from oil and gas production facilities. Spills from unknown sources (132 spills totaling 1,060 tonnes) were not included in the analysis because the source could not be determined. The data were sorted geographically to remove spills to inland waters. Also, only spills of refined petroleum products in coastal areas were included (so as to exclude the crude oil spills from the USCG data base that were included in the section on oil and gas exploration and production). As is the pattern for other sources of spills, facility spills greater than 100 gallons over the period 1990-1999 account for 8.5 percent of the number of spills and 98.3 percent of the spill volume.

Based on the U.S. Coast Guard database of spills greater than 100 gallons over the 10-year period from 1990-1999, there was an average of 119 facility spills per year, with an average volume of 14.4 tonnes each. The average annual spill volume from facilities was 1,708 tonnes. Table G-1 shows the distribution of the number and volume of oil spilled by type of facility. Tables 2-2 through 2-6 shows the distribution of the number and volume of oil spilled by zone.

Two types of facilities were the sources of 66 percent of the oil spilled over the 10-year period: coastal pipelines transporting refined products spilled 33 percent, and marine terminals spilled 33 percent. Industrial facilities were the next largest source of spilled oil, with 14.4 percent. The pipeline spill volume was dominated by one spill event in 1994 where 5,500 tonnes (1,616,000 gallons) of gasoline, crude oil, diesel, and jet fuel were spilled (the San Jacinto River spill in Texas). This one spill accounted for 30 percent of all the oil spilled from facilities in the 10-year period. This spill also demonstrates the problem of how to account for oil removal, since a very large fraction of the spilled oil burned.

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TABLE G-1 Spills from Facilities to Coastal and Marine Waters in the United States, Derived from the U.S. Coastal Guard Data Base for the Period 1990-1999

Spill Source	No. of Spills 1990-1999	Total Spill Volume (Tonnes) 1990-1999	Total Spill Volume (Gallons) 1990-1999
Aircraft/Airports	25	156	44,652
Coastal Pipelines (refined products)	48	5,377	1,565,072
Industrial Facilities	409	2,528	690,053
Marinas	26	63	19,343
Marine Terminals	335	5,727	1,590,378
Military Facilities	55	914	259,500
Municipal Facilities	131	1,181	309,594
Reception Facilities	4	11	3,110
Refineries	56	910	255,698
Shipyards	35	72	19,718
Storage Tanks	44	109	31,361
Other	17	36	10,030
Totals	1,185	17,084	4,798,509

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H

Atmospheric Deposition and Air-Sea Exchange of Petroleum Hydrocarbons to the Ocean

In this analysis, *petroleum hydrocarbons* are defined as consisting of *n*-alkanes between C_{10} and C_{33} chain length and polycyclic aromatic hydrocarbons (PAH). Total hydrocarbon concentrations and loadings are calculated as the sum of these 24 alkanes and 21 PAH. Unburned petroleum contains a myriad of compounds beyond these alkanes and PAH and there are other, nonpetrogenic sources of both of these classes of hydrocarbons. This analysis focuses on these petroleum components because they make up a large fraction of petroleum and because information is available in the literature on their concentrations in marine atmospheres and surface waters and on their physical properties. Though the use of C_{10} through C_{33} alkanes and unsubstituted PAH as total hydrocarbons undoubtedly underestimates the total mass of petroleum loadings, this bias is likely less than two-fold. The second caveat, that nonpetroleum sources of *n*-alkanes and PAH are important, is more problematic. Many species produce and release these hydrocarbons into surface waters and the atmosphere, and *n*-alkane patterns have been used extensively to trace biogenic aerosols over regional and global scales. Many species of plankton produce *n*-alkanes, contributing to the observed levels of these compounds in marine waters. Combustion of biomass and fossil fuels are a substantial source of PAH to the global atmosphere, especially in highly populated areas. While many methods have been proposed to estimate the relative contributions of petrogenic, pyrogenic, and biogenic hydrocarbons to the atmosphere, surface waters, and sediments, the necessary data required to apportion the *n*-alkane levels by source in this analysis were not available. The objective of this analysis is to quantify air-sea exchange of *n*-alkanes and PAH, regardless of their source.

Temporal Scale of Estimates

This analysis began with the data used by Duce and Gagosian (1982) in a National Research Council report. Published literature and known on-going studies were then used to update the estimates of hydrocarbon concentration in the marine atmosphere and in surface waters. Wherever possible, the most recent reliable data were used. The paucity of data often required that all reliable data, regardless of age, be used. Because there are no consistent monitoring programs for hydrocarbons in surface waters or the atmosphere, it is not possible to determine temporal trends in these data. In general, hydrocarbon levels, and therefore loadings, represent conditions in the early- to mid-1990s.

Spatial Scale

This analysis was conducted on two spatial scales. The earlier method used by Duce and Gagosian (1982) in the 1985 NRC report, in which the world's ocean was divided into impacted (Case A) and remote (Case B) zones, was used to estimate hydrocarbon and polycyclic aromatic hydrocarbon (PAH) air-sea exchange worldwide. In addition, the North American coastline was divided into 17 zones, each of which was further divided into zones 0-3 miles and 3-200 miles from shore (For discussion of zones used in this study, see Figure 1-7 and Table B-1) As part of this analysis, each of these zones was described as urban-influenced or rural and assigned consensus values for gas, aerosol particle, and dissolved hydrocarbon and PAH concentrations based on our review of the literature. Deposition was assumed to be uniform within each North American zone and that the concentrations represent annual averages. Assessing seasonality, which certainly influences both the concentrations and depositional processes, was not considered in this analysis.

METHODOLOGY

The general approach used here was similar to that employed by Duce and Gagosian (1982).

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Sources of Data

Ambient gas phase, aerosol-bound and dissolved concentrations of each hydrocarbon in the atmosphere and surface waters of each North American model segment and in the global background were estimated from the current literature. Due to the scarcity of data for the atmospheric petroleum hydrocarbons in the atmosphere bordering North America, the selection of representative distributions of PAH and *n*-alkanes was developed from the current available literature. For this assessment, petroleum hydrocarbons were defined as *n*-alkanes with carbon lengths ranging from C_{10} to C_{33}. To develop an accurate assessment of the contaminant burden to the coastal waters via atmospheric deposition, the various coastal structure and representative contaminant loadings had to be determined. Five zones were assembled based on the degree of urbanization along the zone's shoreline: (1) urban coastline 0-3 miles from shore (U0-3), (2) urban coastline 3-200 miles from shore (U3-200), (3) rural coastline 0-3 miles from shore (R0-3), (4) rural coastline 3-200 miles from shore (R3-200), and (5) background (BG) contaminant levels that would represent the open ocean. In most cases, adjoining 0-3 and 3-200 mile zones had the same designation (rural or urban) except along the west coast of North America, where are 3-200 zones were 'rural' to reflect the predominant westerly air flows off the Pacific Ocean.

Literature on atmospheric hydrocarbons in North America is sparse. This compilation includes those endeavors that have measured concentrations in various selected areas on the United States (Hoff and Chan, 1987; Fraser, 1997; Doskey and Andren, 1986; Foreman and Bidleman, 1990; Ligocki and Pankow, 1989; Mazurek et al., 1991; Simoneit, and Mazurek, 1984). Even fewer atmospheric *n*-alkane data were available for the North American coast that reported vapor phase alkanes per homologue (Fraser, 1997, 1998; Hoff, 1987). Sampling methods were somewhat consistent throughout the literature. All of the authors use a high-volume air sampler to pull ambient air at specified flow rates through a sample train that contains a glass or quartz fiber filter to retain atmospheric particles. When the vapor phase is collected, a polyurethane plug or PUF is placed beyond the filter in the sampling train. Doskey and Andren (1986) deviated from this format by using XAD-8 resin to collect the vapor phase *n*-alkanes. Lighter hydrocarbons can also be collected using an evacuated stainless steel canister filled with ambient air and directly injected into a gas chromatograph via sorbent thermal desorption (Fraser, 1997). Sample preparation usually involved the extraction of the filter, PUF or XAD with nonpolar organic solvent by soxhlation or sonication. Extracts may be fractionated over an alumina silicic-acid column (Foreman and Bidleman, 1990; Cotham and Bidleman, 1995) or applied to thin-layer chromatography (Daisey et al., 1981) to separate alkanes. The various forms of instrumentation used in the quantification of hydrocarbons ranged from high performance liquid chromatography coupled with a fluorescence detector (Daisey, 1981; Foreman and Bidleman, 1990) and confirmed by GC/MS (Foreman and Bidleman, 1990) or secondary spectroscopic techniques (Daisey et al., 1981). While Doskey and Andren, (1986) quantified their extracts using gas chromatography equipped with a flame ionization detector, the remainder of the most recent work relies on the resolving power of gas chromatography and the instant confirmation of mass selective detector technology (Hoff and Chan, 1987, Baker and Eisenreich, 1990; Cotham and Bidleman, 1995; Fraser et al., 1997, 1998; Offenberg, 1998; Bamford et al., 1999a; Giglitotti et al., 2000).

The data set acquired from Hoff (1987) collected along the Niagara River between Lake Erie and Ontario, contained values for C16, C22, C24, and C28 *n*-alkanes in the vapor and particulate phase. Fraser et al., (1997) performed a thorough analysis of the distribution of various hydrocarbons in California during a photochemical smog episode. Aerosol and vapor phase data were taken from San Nicolas Island, Long Beach, central Los Angeles, Azusa, and Claremont. Gaseous and particulate samples were taken using a standard high volume air sampler fitted with a quartz fiber filter (aerosols) and polyurethane plug (vapor). Concurrent gas samples were also taken with 6-L stainless steel canisters. Reported concentrations for the filters, PUF, and canister samples ranged from C18 to C36, from C14 to C28, and from C2 to C13 alkane homologues, respectively. There seems to be some discrepancy between the canister and PUF concentration values from C13 to C14. This may be due to breakthrough of the lighter alkanes in the PUF portion of the high-volume sampler, which consisted of a series of five PUF plugs in series. Separate analysis of the individual PUF plug series showed that the last PUF contained no more than 15 percent of the total alkanes collected on the previous four, which does not explain the factor of 10 difference between the C13 (canister) measurement and the C14 (PUF) measurement. Despite these discrepancies, this data set constitutes the most expansive coverage of the alkane distribution along the urbanized North American coast. The mean of the four coastal California cities, Long Beach, central Los Angeles, Azusa, and Claremont, has been selected to represent the highly impacted coastline of North America in terms of alkane vapor and particulate concentrations (U0-3). San Nicolas Island, which lies approximately 100 km west of the California coast, will constitute the typical atmospheric concentrations offshore (3-200 miles) of a highly urbanized coastline (U3-200).

A second, urbanized coastline alkane distribution was also selected. For the purpose of this analysis Los Angeles, California, is considered to represent an extreme example of an urbanized coastline. Thus, a second alkane distribution, representative of a less urbanized area, was needed. As no well-documented coastal setting was available, this analysis uses data obtained from an interior urban center. Denver,

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Colorado was thus selected as being reflective of a more moderately impacted urban area. Foreman and Bidleman (1990) characterized the Denver atmosphere for alkanes. The authors note the major sources of airborne contaminants in the Denver area may be due to coal-driven electric power generation and wood burning, unlike Los Angeles, where the mean concentrations found by Fraser (1997) in southern California incorporate several alkane sources, from dense automobile traffic from major freeways to active shipping ports. For the purposes of this study the southern California levels will be retained as a highly impacted urban coastline with the note that nonrural, urban coastlines may more accurately be reflected in the Denver alkane distribution.

The rural sectors of the coastline are expected to have less of a petrogenic alkane signal. Doskey and Andren (1986) conducted a study in northern Wisconsin approximately 200 km from urbanization (Green Bay, Wisconsin) and 4.5 mils from any major roadway. Similar methods of sampling were performed, as mention above, using a high-volume sampler fitted with a filter and gaseous sorbent. The PUF was replaced with XAD-2 resin for the collection of vapor alkane constituents. Winter total alkanes were taken from this study to minimize the biogenic contribution via plant waxes from spring pollen that may falsely elevate hydrocarbon concentrations in a rural environment. Rural offshore (R3-200 and BG) particulate phase alkane levels were obtained from an expansive aerosol characterization endeavor performed along the western U.S. coast by Simoneit (1982). Aerosol samples were collected from Crater Lake, Oregon. These particulate values were chosen due to the low value obtained and the remote nature of the sampling site. Totals were also only reported for this particular sampling site. The distribution was back calculated using the alkane distribution from Fraser et al. (1997).

The rural areas consisted of the northern Chesapeake Bay (Offenberg, 1998; Leister and Baker, 1994; Dickhut and Gustafson, 1995) Isle Royal, Lake Superior (McVeety and Hites, 1988); and Sandy Hook, New Jersey (Gigliotti et al., 2000). Isle Royal, the main island in Lake Superior, represents a remote signal; the winds are predominantly from the west, and the nearest urban center is approximately 300 km from the sampling site. Sandy Hook, New Jersey, lies on a peninsula approximately 10 km south of New York and 30 km southeast of Newark, lending to direct urban influence and from elevated populations to the west, south, and southwest (Gigliotti et al., 2000). The rural coastal compartment (R0-3) can be best characterized by the sampling performed on the eastern shore of the northern Chesapeake Bay (Offenberg, 1998). No observable urban influence (via Baltimore) was observed from air parcels from Baltimore, the nearest urban center. Therefore this station has minimal urban influence, representative of a rural coastline. The offshore rural or background values (BG) were selected from Ellsmere Island and Alert, Canada, and Tangish in the Yukon Territories (Hallsall et al., 1997; Fellin et al., 1996); Barrow, Alaska (Daisey et al., 1981); Narwahl Island (Daisey et al., 1981); and Isle Royal, Lake Superior (McVeety and Hites, 1988).

VOC Emissions

Crude oils contain a variety of volatile organic compounds (VOC) that evaporate quickly into the atmosphere. Significant quantities of VOC can be released during cargo loading and unloading, during transport, and during crude oil washing operations on board crude oil carriers. Methane makes up approximately 80 percent of these VOC emissions. Methane released into the atmosphere will not deposit, and while it may be a "greenhouse gas" concern, does not appreciably impact the volume of oil entering the sea. Of the remaining VOC, only a small fraction is likely deposited to the sea, as detailed later in this chapter.

Precise measurement of VOC loss from tankers is difficult. The best measure currently available is derived from the fact that cargo insurance companies will typically exclude coverage for loss of 0.5 percent of a crude oil cargo as normal variation between loading and unloading ports. This is the upper range of potential uncovered loss, and it is generally assumed that average loss is probably about half that amount or 0.25 percent most of which can be attributed either to cargo tank gauging variations or, more likely, to VOC emissions.

Approximately 3.3 billion tonnes of cargo oil was moved on tank vessels in 1999. Thus, VOC emissions during crude oil shipment can be estimated as follows:

billion tonnes • 0.0025 tonnes lost/tonne shipped = 8,250,000 tonnes

The VOC emissions (heavier than butane) are therefore:

8,250,000 tonnes • 0.2 non-methane tonnes/tonne = 1,650,000 tonnes

This is a worldwide estimate from shipping. The best estimate of VOC emissions (heavier than butane) from platforms in coastal North American waters is 60,000 tonnes, and the worldwide estimate is 649,000 tonnes (see Section B).

Deposition Calculations

Deposition models were used to estimate depositional fluxes (mass deposited per unit area per year) from these concentrations, and these fluxes were integrated over the area of each model segment to calculate the annual loading. Equations used in these calculations are shown in Figure H-1 and have been used extensively to estimate exchange of semivolatile organic chemicals between the atmosphere and surface waters (Baker and Eisenreich, 1990; Iwata et al., 1993; Achman et al., 1993; Hornbuckle et al., 1994; 1995; Nelson et al., 1998; Bamford et al., 1999a,b; Zhang et al.,

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1999; Harman-Fetcho et al., 2000; Bamford et al., 2000). Wet deposition results from the scavenging of gases and particles, which were modeled from the temperature-corrected Henry's law constant and the aerosol scavenging ratios, respectively (Equations A-1 through A-3). Henry's Law constants for the hydrocarbons are identical to those used by Duce and Gagosian (1982). Each Henry's law constant was corrected to 11° C using the enthalpies of phase change reported by Bamford et al., (1999a, 2000), as detailed in Equation C-6. Global annual precipitation was assumed to be 100 cm/year. While spatial and temporal variability in temperature and precipitation rate will alter atmospheric deposition rates, any bias resulting from using uniform global temperature (11° C) and precipitation rates here is likely within the error of these estimates.

Dry aerosol deposition fluxes were calculated as the product of the estimated aerosol-bound hydrocarbon and the dry deposition velocity (Equation B-1). Estimates of deposition velocity range from <0.01 cm/sec to >1 cm/sec and depend on particle size, relative humidity, and surface turbulence. Most studies of organic chemical dry aerosol deposition suggest a deposition velocity in the range of 0.1 cm/sec is conservative. For this analysis, a deposition velocity of 0.1 cm/sec was used, corresponding to a 0.5-μm particle depositing under average wind conditions. Annual dry deposition velocity was assumed to be spatially invariant.

Gross gas absorption deposition fluxes were calculated by dividing the estimated gas phase hydrocarbon concentrations by their respective temperature-corrected dimensionless Henry's law constants and multiplying the result by the air-sea exchange mass transfer coefficient (Equations C1-C12). The mass transfer coefficient for each compound was estimated using the two-film model, using relationships between wind speed and tracer exchange rates to parameterize surface turbulence and the compound-specific diffusivities and Henry's law constants (see Nelson et al., 1997, and Bamford et al., 1999 for details of this calculation). Gross gas deposition fluxes are only one-half of the net bidirectional diffusive exchange of gases across the air-water interface. The corresponding gross volatilization fluxes for each compound were calculated as the product of the estimated dissolved phase hydrocarbon concentration and the air-sea mass transfer coefficient described above (Equation D-1). Since the analysis is calculating loads from the atmosphere to the ocean, volatilization fluxes are negative by convention.

Deposition of Fugitive Emissions From Tankers and Production Platforms

For fugitive emissions from tankers (loss of volatile product during transport) and emissions of volatile species from platforms, see Section B), a simple box model calculation is used to estimate the fraction of the emission that may be deposited into the surface waters. While the exact composition of volatile organic carbon (VOC) lost by volatilization is poorly known, it is very likely that it is dominated by one to three carbon hydrocarbons that are significantly more volatile than the C_{10} to C_{33} *n*-alkanes considered in this report. To assess the potential loading of hydrocarbons from fugitive emissions of VOC, this analysis considers the following conservative calculation. We assume (1) that 80% of the VOC released from tankers is methane and other light hydrocarbons that do not deposit to the sea surface; (2) that the remaining VOC mix (20% of total VOC emitted from tankers) has a Henry's law constant equal to that of decane (which certainly underestimates its volatility and, therefore, overestimates deposition); (3) that the released VOC do not react in the atmosphere or in surface waters (which ignores the substantial degradation due to hydroxyl radical attack in the troposphere); and (4) that the released VOC rapidly partition between the atmosphere, which is well mixed to 1000 m altitude, and the surface ocean, which is well mixed to 100 m depth. Ignoring the substantial atmospheric reactions and using the physical properties of decane result in a very conservative calculation, likely overestimating hydrocarbon loadings to the oceans from these sources. Under this simple scenario, equilibrium calculations show that less than 0.2 percent of the released VOC are deposited to surface waters, even under these very conservative conditions. Based on the VOC emissions of 60,000 metric tonnes (VOC heavier than butane) to North American coastal waters from production platforms (Section B), on the order of 120 metric tonnes (60,000 tonnes x 0.002 tonnes deposited/tonne released) of VOC may enter the coastal ocean as a result of VOC release from platforms. This compares to the 2,100 metric tonnes of hydrocarbons calculated to enter the North American coastal ocean (0-200 miles) from the atmosphere (see below). VOC emissions (heavier than butane) from tankers during loading, transit, and offloading worldwide (1,650,000 tonnes) may result in a VOC loading of 3,300 metric tonnes globally.

Calculation of Total Net Loads

Annual total net loads of individual hydrocarbons were calculated as the sum of wet and dry aerosol deposition and gas absorption minus gross volatilization, integrated over the area of each zone. Total hydrocarbon loads were calculated as the sum of C_{10} to C_{33} *n*-alkanes. Finally, total loads for North American waters and the world's oceans were calculated by summing the loads to the component areas.

ESTIMATES OF ATMOSPHERIC DEPOSITION LOADINGS OF PETROLEUM HYDROCARBONS TO THE OCEAN

Based on the data and methodologies detailed above, wet, dry aerosol, gas absorption, and volatilization fluxes for each of the hydrocarbons were determined (contact NRC staff to

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obtain detailed information describing how specific determinations were made, including initial data and intermediate calculated values for individual compounds of interest). Globally, wet deposition and dry aerosol deposition supply 43,000 and 13,600 metric tonnes of C_{10} to C_{33} *n*-alkanes to the ocean, respectively. This estimate of 56,600 metric tonnes is within the range of 40,000 to 400,000 metric tonnes reported earlier by Duce and Gagosian, (1982). Most importantly, this loading is overwhelmed by the volatilization of 3,000,000 metric tonnes of these compounds. Clearly these results indicate that the world's oceans are a net source of hydrocarbons to the atmosphere, where they are transported globally and degraded. In North American coastal waters, 16,000 and 5,030 metric tonnes of C_{10} to C_{33} *n*-alkanes are delivered from the atmosphere to the water's surface, and 1.76 million metric tonnes volatilize (See Table H-1). It is apparent that terrestrial hydrocarbon loadings and near shore sources support dissolved hydrocarbon loadings in coastal waters that far exceed that in equilibrium with the atmosphere. Hydrocarbon degassing from coastal waters is a major geochemical process.

TABLE H-1 Summary of Alkanes and PAH Included in Net Annual Atmospheric Deposition Calculations

Alkanes	PAH
C-10	Naphthalene
C-11	Acenapthylene
C-12	Fluorene
C-13	Phenanthrene
C-14	Anthracene
C-15	Fluoranthene
C-16	Pyrene
C-17	Benzo[a]fluorene
C-18	Benzo[b]fluorene
C-19	Benz[a]anthracene
C-20	Chrysene/Triphenylene
C-21	Benzo[k]fluoranthene
C-22	Benzo[b]fluoranthene
C-23	Benzo[e]pyrene
C-24	Benzo[a]pyrene
C-25	Perylene
C-26	Indeno[1,2,3-cd]pyrene
C-27	Indeno[1,2,3-cd]fluoranthene
C-28	Dibenz[ah]anthracene
C-29	Benzo[ghi]perylene
C-30	Coronene
C-31	
C-32	
C-33	

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TABLE H-2 Calculated Net Annual Atmospheric Deposition Loadings to Each Geographic Zone, Tonnes/Year

Zone	Area (m^2)	Zone Type	Alkanes	PAH	Total By Zone
Global Case A	8.0E+13	Case A	–2,177,515	–14,253	–2,191,768
Global Case B	2.8E+14	Case B	–865,923	–4,989	–870,912
A 0-3 miles	1.7E+11	R3	–41,149	38	–41,111
A 3-200 miles	1.9E+12	R200	–33,709	42	–33,667
B 0-3 miles	1.1E+11	R3	–27,273	25	–27,248
B 3-200 miles	1.9E+12	R200	–34,028	42	–33,985
C 0-3 miles	7.6E+10	R3	–18,795	17	–18,778
C 3-200 miles	1.3E+12	R200	–24,137	30	–24,107
D 0-3 miles	2.4E+10	U3	–195,398	1	–195,398
D 3-200 miles	3.8E+11	U200	–97,813	45	–97,768
E 0-3 miles	1.7E+10	U3	–138,365	1	–138,364
E 3-200 miles	7.7E+11	U200	–197,633	90	–197,543
F 0-3 miles	8.7E+09	U3	–70,175	0	–70,175
F 3-200 miles	3.6E+11	U200	–92,366	42	–92,324
G 0-3 miles	1.4E+10	U3	–110,435	1	–110,435
G 3-200 miles	2.6E+11	U200	–67,579	31	–67,548
H 0-3 miles	1.4E+10	U3	–113,761	1	–113,760
H 3-200 miles	7.8E+11	U200	–200,888	92	–200,796
I 0-3 miles	4.0E+09	R3	–1,003	1	–1,002
I 3-200 miles	6.1E+11	R200	–11,010	14	–10,996
J 0-3 miles	3.5E+10	R3	–8,606	8	–8,599
J 3-200 miles	1.2E+12	R200	–21,460	27	–21,433
K 0-3 miles	2.1E+09	U3	–16,764	0	–16,764
K 3-200 miles	6.3E+10	R200	–1,155	1	–1,154
L 0-3 miles	6.5E+09	U3	–52,498	0	–52,497
L 3-200 miles	3.3E+11	R200	–6,060	105	–5,955
M 0-3 miles	1.0E+10	R3	–2,501	2	–2,499
M 3-200 miles	2.8E+11	R200	–5,053	6	–5,046
N 0-3 miles	2.3E+10	R3	–5,672	5	–5,667
N 3-200 miles	3.1E+11	R200	–5,711	7	–5,704
O 0-3 miles	1.2E+10	R3	–70	3	–67
O 3-200 miles	3.2E+12	R200	–58,156	72	–58,084
P 0-3 miles	7.3E+10	R3	–18,123	17	–18,106
P 3-200 miles	1.8E+12	R200	–31,926	40	–31,886
Q 0-3 miles	4.8E+10	R3	–11,836	11	–11,825
Q 3-200 miles	1.9E+12	R200	–34,621	43	–34,578
North America Total			–4,799,167	–18,383	–4,817,550

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A. Wet Deposition

A-1 $$J_{wet} = J_p \quad [W_g C_g \quad W_a C_a]$$

Where J_p = Annual precipitation (m^3/m^2yr)
W_g = gas phase scavenging coefficient (dimensionless)
W_a = aerosol phase scavenging coefficient (dimensionless)
C_g = gas phase hydrocarbon concentration (ng/m^3)
C_a = aerosol phase hydrocarbon concentration (ng/m^3)

A-2 $W_g = RT/H$

Where R = ideal gas constant ($8.21 \times 10^{-5} m^3 \cdot atm/mol.deg$)
T = absolute temperature
H = temperature corrected Henry's Law Constant ($atm.m^3/mol$)

A-3 $W_a = 10^5$(assumed constant. Set to match observations in Poster and Baker, 1996)

B. Dry Aerosol Deposition

B-1 $J_{dry\ aerosol} = V_d C_a$

Where V_d = aerosol deposition velocity (m/yr) assumed constant at 0.1 cm/sec = 31,536 m/yr

C. Gross Gas Absorption

C-1 $$J_{gas\ abs.} = K_{OL} \quad \frac{C_g RT}{H} \quad (365\ d/yr)$$

Where K_{OL} = overall air-water mass transfer coefficient (m/day)

C-2 $$\frac{1}{K_{OL}} \quad \frac{1}{k_a[\frac{RT}{H}]} \quad \frac{1}{k_w}$$

Where k_a = air side mass transfer coefficient (m/day)
k_w = waterside mass transfer coefficient (m/day)

C-3 $$k_{a,HC} \quad k_{a,H_2O} \quad (\frac{D_{HC,AIR}}{D_{H_2O,AIR}})^{0.61}$$

FIGURE H-1 Equations used to generate estimate of input of petroleum to the marine environment from atmospheric sources.

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FIGURE H-1 Continued

C-4 *Where* k_{a,H_2O} $0.2U_{10}$ 0.3

U_{10} *windspeed at* 10*m*

$D_{HC,Air}$ = diffusivity of the hydrocarbon in air

$D_{H2O,Air}$ = diffusivity of water vapor in air

C-5 $$D_{HC,Air} \quad \frac{T^{1.75}\left(\frac{1}{MW_{Air}} \quad \frac{1}{MW_{HC}}\right)^{1/2}}{(V_{m,air} \quad V_{M,HC})^{2/3}}$$

Where MW_{Air} = molecular weight of air = 28.97 g/mole

MW_{HC} = molecular weight of hydrocarbon

$V_{m,air}$ = molar volume of air

$V_{m,HC}$ = molecular volume of hydrocarbon (cm^3/mol)

C-6 $$\ln \frac{H}{RT} \quad \frac{!\,H}{RT} \quad !\,S/R$$

Where! H = Enthalpy of dissolved-gas phase change (kJ/mol)

! S = Entropy of dissolved-gas phase change (kJ/molK)

C-7 $$k_{W,HC} \quad k_{W,CO_2}\left(\frac{SC,HC}{SC,CO_2}\right)^{1/2}$$

C-8 where k_{w,co_2} $0.45\,U_{10}^{1.64}$

Sc_{HC} = Schmidt number of hydrocarbon

Sc_{CO_2} *Schmidt number of* CO_2

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C-9 $Sc_{HC} \quad \frac{\mu_T}{"_{H_20} \; D_{HC,H_20}}$

Where μ = absolute viscosity of water (g/cm-s)

" = density of water (g/cm^3)

$D_{HC,H2O}$ = diffusivity of hydrocarbon in water.

C-10 $\mu_T = -2.778 \text{ X } 10^{-4}T + 0.0164 \; (T=°C)$

C-11 $"_{H_2O} \quad 1.899 \, x \, 10^{4} T \quad 1.0011 \; (T=°C)$

C-12 $D_{HC,H_2O} \quad \frac{1.326 \; x \; 10^{4}}{(100\mu_T)^{1.14} V_{M,HC}^{0.589}}$

D. Gross Volatilization

D-1 $J_{VOL} = K_{OL} \, C_d \, 365$

Where C_d = dissolved hydrocarbon concentration (ng/m^3)

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I

Estimating Land-based Sources of Oil in the Sea

Because of the scarcity of available data for estimating land-based loads of oil to the sea from individual sources (i.e., municipal wastewaters, nonrefinery industrial discharge, refinery discharges, urban runoff, river discharges, and ocean dumping), loading estimates presented in this analysis were based on loading from all land-based sources per unit of urban land area. These calculations assumed that most of the contributions of petroleum hydrocarbons to the sea from land-based sources were from urban areas. This approach accounted for loading from all of the sources in the United States and Canada, with the exception of Gulf coast loadings from coastal refineries, which was calculated separately. The overall calculations of hydrocarbon loadings from all land-based sources for the United States and Canada were then extrapolated to other regions of the world to form a world estimate.

METHODOLOGY AND SOURCES OF THE DATA

A review of the U. S. Environmental Protection Agency's STORET data base revealed oil and grease data for only nine major rivers in the United States, and several of these consisted of very few observations. Even fewer rivers (i.e., Brazos, Delaware, and Trinity) had hydrocarbon data. The dominance of oil and grease data measured using either the Soxhlet extraction method (tot-sxlt) or liquid-liquid extraction (freon-gr) methods in the available STORET data led to the use of measured oil and grease concentrations as the basis for estimates presented in this analysis.

Quantified estimates of oil and grease and petroleum hydrocarbon loadings were made for the United States and Canada. These estimates were made using unit loadings per urban land area. The annual loadings were calculated according to the coastal zones defined in this study, and the overall loadings for the United States and Canada were extrapolated to the world.

For the calculations in the United States and Canada, the land-based sources were divided into two categories: inland basins and coastal basins. It was assumed that inland basins discharged into one of the following major river basins that outlet to the sea along the coast of the United States and Canada (coastal basins were assumed to discharge directly to the sea):

- Alabama-Tombigbee
- Altamaha
- Apalachicola
- Brazos
- Colorado (Texas)
- Columbia
- Copper (Arkansas)
- Delaware
- Hudson
- James
- Mississippi
- Neuse
- Potomac
- Rio Grande
- Roanoke
- Sabine
- Sacramento
- St. Lawrence
- Santee
- San Joaquin
- Saskatchewan
- Savannah
- Susitna
- Susquehanna
- Trinity
- Yukon

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Calculations for the Inland Rivers of the United States and Canada

The following methodology was used to estimate the loading of oil and grease to the sea from inland river basins in the United States and Canada:

1. The location of the mouth of each river was determined on a map. These locations were then expanded into regions of interest (generally defined by the latitude and longitude of the lowest U.S. Geological Survey (USGS) gauging station and a radius around that point; see Table I-1) for which water quality data were requested from STORET. Searches were made for all surface water quality data collected within these regions.

   Data for the following parameter codes were then requested from STORET if they were included in the data summaries for the regions:

   - Parameter code 00550: oil-grse tot-sxlt (mg L^{-1})
   - Parameter code 00552: oil-grse tot-hexn (mg L^{-1})
   - Parameter code 00556: oil-grse freon-gr (mg L^{-1})
   - Parameter code 00560: oil-grse freon-ir (mg L^{-1})
   - Parameter code 03582: oil and grease tot wtr (mg L^{-1})
   - Parameter code 45501: hydrocarbon ir (mg L^{-1})

2. Averages of all reported values in STORET for the parameter codes listed were compiled for each river (Table I-2) with the following assumptions (rivers not shown in Table I-2 did not have any usable oil and grease data):
   - Only 'ambient' readings in freshwater rivers were included; this means that values reported for industrial or municipal effluents, nonambient conditions, sediment, and/or ocean/estuary locations were not included in the average.
   - Some values were reported to be 'off-scale low,' which meant that the actual value was not known, but was known to be less than the value shown. To calculate our averages, we set these values to one-half their reported value.
   - For those rivers with data in the 1990s, average concentrations for that period were calculated.

3. An average annual load in tonne yr^{-1} was calculated for those rivers with reported oil and grease data by using the following formula:

TABLE I-1 Regions Searched for Oil and Grease and Hydrocarbon Data from STORET

River	Latitude	Longitude	Radius (mi)
Alabama-Tombigbee	32°00′00″, 30°00′00″	–87°15′00″, –88°15′00″	See note[a]
Altamaha	32°31′30″	–81°15′45″	50
Apalachicola	See note [b]		
Brazos	29°34′56″	–95°45′27″	50
Colorado (TX)	28°58′26″	–96°00′44″	30
Columbia	46°10′55″	–123°10′50″	50
Copper (AK)	61°00′00″	–144°45′00″	50
Delaware	39°30′03″	–75°34′07″	30
Hudson	41°43′18″	–73°56′28″	40
James	37°24′00″	–77°18′00″	50
Mississippi	29°16′26″	–89°21′00″	50
Neuse	35°06′33″	–77°01′59″	50
Potomac	38°55′46″	–77°07′02″	75
Rio Grande	25°52′35″	–97°27′15″	30
Roanoke	35°54′54″	–76°43′22″	70
Sabine	30°18′13″	–93°44′37″	50
Sacramento	37°30′00″, 38°30′00″	–121°00′00″, –123°00′00″	See note[a]
St. Lawrence	45°00′22″	–74°47′43″	50
Santee	33°14′00″	–79°30′00″	40
San Joaquin	37°30′00″, 38°30′00″	–121°00′00″, –123°00′00″	See note[a]
Saskatchewan	See note[b]		
Savannah	32°31′30″	–81°15′45″	50
Susitna	61°35′00″	–150°22′00″	40
Susquehanna	39°42′00″	–76°15′00″	50
Trinity	29°50′10″	–94°44′57″	30
Yukon	62°45′00″	–164°30′00″	30

NOTES: [a]Rectangular polygons formed by the latitudinal and longitudinal coordinates shown were requested for these rivers; [b]No data were requested for the Appalachicola and Saskatchewan Rivers.

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TABLE I-2 STORET Data Used to Calculate Average Oil and Grease Concentrations in Major Inland Rivers

River	Station name	Parameter code	# of observations	Date(s) of observations	Average concentration (mg L^{-1})
Columbia	Columbia River at Bradwood, OR	00550	27	4/24/74–10/17/78	1.80
Delaware	Delaware Rvr-2000 yds up buoy R6M-Marcus Hook	00556	107	5/23/88–12/29/98	6.00
Delaware (1990s)	Delaware Rvr-2000 yds up buoy R6M-Marcus Hook	00556	99	1/22/90–12/29/98	5.80
Hudson	Hudson River below Poughkeepsie, NY	00550	2	6/4/70–9/7/71	60.50
James	Buoy 8 (City of Hopewell)	00556	1	7/20/92	19.30
Mississippi	Mississippi River at Venice, LA	00556	229	10/4/73–11/19/96	1.74
Mississippi (1990s)	Mississippi River at Venice, LA	00556	46	1/11/90–11/19/96	0.84
Neuse	Neuse River at 3 locations	00550	7	6/6/73–6/7/73	0.00
Sabine	Sabine River at Ruliff, TX	00556	45	3/27/74–5/9/78	2.50
Sacramento	Sacramento River at Freeport, CA	00550	4	10/25/91–2/2/92	0.83
Susquehanna	Susquehanna R at Rte 40 bridge	00500	2	8/3/78	0.00
Trinity	Trinity River at Liberty, TX	00550	11	5/4/71–8/31/72	8.18

Equation I-1

$$L_i = c_i Q_i,$$

where L_i = average annual load for river i (tonne yr^{-1}),
c_i = average oil and grease concentration for river i (mg L^{-1}),
Q_i = average annual flow for river i (m^3 yr^{-1}),
tonne = 10^6 g.

The average annual flow (per calendar year) was determined from USGS daily flow data available for each of the rivers at the nearest nontidally influenced station to that of the reported oil and grease data (Table I-3). For calculations of loads using average concentrations in the 1990s only, average annual flows for those rivers were calculated using only daily flow data from the 1990s.

4. Using data obtained from the U.S. Bureau of the Census (1998), unit loads per urban land area were calculated as follows:

Equation I-2

$$l_{ai} = \frac{L_i\left(10^6 \frac{g}{\text{tonne}}\right)}{A_{ui}}$$

where lai = unit load per urban land area for river i (g m^{-2} yr),
Aui = 1996 urban land area for river i (m^2).

The 1996 urban land area in each river basin was determined by using Table I-1 in U.S. Bureau of the Census (1998), which contained land area data for metropolitan areas defined as of June 30, 1996. Metropolitan areas in this table were partitioned into the major river basins identified in Table I-1, coastal areas, the Great Lakes, or areas not discharging to the coast of the United States or Canada (e.g., Great Salt Lake basin). Metropolitan areas contributing urban runoff to the Great Lakes or areas not discharging to the coast of the United States or Canada were not included further in the analysis. It was assumed that oil and grease dis-

TABLE I-3 USGS Gages Used to Calculate Average Annual Flows for Major Inland Rivers

River	Station name	Period of record used	Average annual flow (m^3 yr^{-1})
Columbia	14246900: Columbia R at Beaver Army Terminal nr Quincy, Ore	1969, 1992-1997	220,892,000,000
Delaware	01463500: Delaware River at Trenton, NJ	1913-1997	10,441,000,000
Delaware (1990s)	01463500: Delaware River at Trenton, NJ	1990-1997	10,712,000,000
Hudson	01358000: Hudson River at Green Island, NY	1947-1996	12,365,000,000
James	02037500: James River near Richmond, VA	1938-1997	6,209,000,000
Mississippi	07289000: Mississippi River at Vicksburg, MS	1932-1997	537,114,500,000
Mississippi (1990s)	07289000: Mississippi River at Vicksburg, MS	1990-1997	625,760,000,000
Neuse[a]	02089500: Neuse River at Kinston, NC	1983-1997	3,524,394,745
Sabine	08030500: Sabine River nr Ruliff, TX	1960-1997	7,043,181,292
Sacramento	11447650: Sacramento River at Freeport, CA	1949-1997	21,000,000,000
Susquehanna	01578310: Susquehanna River at Conowingo, MD	1968-1997	36,779,000,000
Trinity[b]	08067000: Trinity River at Liberty, TX	1977, 1979-1986	8,944,000,000

NOTES: [a]adjusted to Station 02091814 using 1997 data; [b]missing flows regressed with Station 08066500: Trinity River at Romayor, TX (y = 0.8559x + 4047.8).

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charged to the Great Lakes would be biochemically reduced, or would attach to solids and settle out during the extended residence time in the lakes and would therefore not make it to the ocean. Likewise, closed inland basins such as the Great Salt Lake would not discharge to the sea. (Contact NRC staff to obtain information describing how specific metropolitan areas were classified as contributing to major river basins.)

5. For the majority of the inland river basins, no usable oil and grease data were available in STORET. In addition, the number of observations for the Hudson, James, Neuse, Sacramento, and Susquehanna rivers was very small (2, 1, 7, 4 and 2, respectively). It was therefore decided to use an alternative procedure based on the unit loads of oil and grease per urban land area and per capita calculated from Steps 1-4 to estimate the contributions of oil and grease from these other river basins. The procedure was as follows:

a. The unit loads of oil and grease per urban land area calculated from Steps 1-4 were used for the other river basins with the following assumptions:

   - The Hudson and James rivers were assumed to have unit loads of oil and grease per urban land area of 12.22 g m^{-2} yr^{-1}, the values calculated from 99 observations in the 1990s on the Delaware River. The high unit loadings on the Delaware River are likely due to the highly industrialized nature of the waterway, and the Hudson and James rivers are also very industrialized.
   - It was assumed that Alaskan rivers (i.e., Copper, Susitna, and Yukon rivers) did not contribute significant loads of oil and grease to the ocean.
   - All other rivers for which measured data were not adequate or were unavailable were assumed to have unit loads of oil and grease per urban land area of 1.25 g m^{-2} yr^{-1}. This value was based on the average annual loading for 1990s data from the Mississippi and Delaware rivers together divided by the urban areas in both basins. Rivers for which this value applied included the Alabama-Tombigbee, Altamaha, Apalachicola, Brazos, Colorado (Texas), Columbia, Neuse, Potomac, Rio Grande, Roanoke, Sabine, Sacramento, St. Lawrence, Santee, San Joaquin, Saskatchewan, Savannah, Susquehanna, and Trinity rivers.

b. Using data obtained from the U.S. Bureau of the Census (1998) and Statistics Canada (2000), the annual loads per unit land area (Lai) were calculated as follows:

Equation I-3

$$L_{ai} = l_{ai} A_{ui} \left(\frac{\text{tonne}}{10^6 g} \right)$$

where *lai* was the unit load for river *i* as described in Step 5.a. The urban land area, *Aui*, was calculated in the same manner as described in Step 4 for metropolitan areas in the United States. For metropolitan areas in Canada, *Aui* was calculated using data from Statistics Canada (2000).

Calculations for the Coastal Zones of the United States and Canada

For the United States, metropolitan areas in U.S. Bureau of the Census (1998) were classified as contributing to coastal basins if they fell within one of the 451 coastal counties defined by Culliton et al. (1990). The individual coastal basin metropolitan areas were then aggregated into the appropriate coastal zones in Figure 1-7. The data for 1997 urban land area for metropolitan areas as of June 30, 1996 (U.S. Bureau of the Census, 1998) were then compiled for each coastal zone. Similarly, data from Statistics Canada (2000) for Canadian metropolitan areas along the coast were grouped into the appropriate coastal zones.

The annual load *Lai* was calculated for urban areas in each coastal zone *i* in the United States and Canada using Equation I-3. The unit load per urban land area for coastal zone *i*, *lai*, was 12.22 g m^{-2} yr^{-1} for coastal zone D, and 1.25 g m^{-2} yr^{-1} for all other coastal zones. The unit loads were set at higher values for Coastal Zone D because that is the coastal zone to which the Delaware River discharges. (Contact NRC staff to obtain information describing how specific metropolitan areas were classified as contributing to various coastal zones.)

Because almost one-fourth of the crude oil distillation capacity of the United States is located along the Gulf coast (Radler, 1999), the petroleum refining industry discharges a substantial amount of additional oil and grease to coastal waters in that area. To estimate this contribution, data for oil refineries in Louisiana and Texas (from Radler, 1999) were used to estimate the operating capacity of coastal refineries in these states (Table I-4). The petroleum hydrocarbon discharge was determined by multiplying the operating capacity by an assumed rate of hydrocarbon loss that corresponded to effluent guidelines for these discharges (American Petroleum Institute, National Ocean Industries Association, and Offshore Operators Committee, 2001):

Daily maximum:	6.0 lbs per 1000 barrels of crude produced
Monthly average:	3.2 lbs per 1000 barrels of crude produced

Calculations using each of these guidelines were made, and the average of the two calculations was used as a best estimate of the loadings. This discharge was added to the coastal discharge for coastal zone G.

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TABLE I-4 Estimated Petroleum Hydrocarbon Discharge to Gulf Coast from Petroleum Refining Industry

State	No. of Operable Refineries on Coast[a]	Crude Distillation Capacity[a] (bbl d^{-1})	Crude Distillation Capacity[b] (10^6 tonne yr^{-1})	Oil and Grease Discharge—Low[c] (tonne yr^{-1})	Oil and Grease Discharge—High[d] (tonne yr^{-1})	Oil and Grease Discharge—Average[e] (tonne yr^{-1})
Texas	14	2,836,100	125466.7	1,503	2,160	2,817
Louisiana	7	948,105	124210.5	502	722	942
TOTAL	21	3,784,205		2,005	2,882	3,759

NOTES: [a]SOURCE: Radler (1999); [b]10^6 tonne yr^{-1} = 19,000 bbl d^{-1}; [c]assuming 3.2 lbs of oil and grease are produced per 1000 bbl produced; [d]assuming 6.0 lbs of oil and grease are produced per 1000 bbl produced; [e]average of low and high estimates.

The total oil and grease loading was determined by adding discharges from inland rivers, urban coastal areas, and the petroleum refinery discharges in the Gulf of Mexico to the appropriate coastal zones.

World Estimates of Oil and Grease

The data used for the calculations of oil and grease loading for North America were not available for other regions of the world. Therefore, a method was needed to extrapolate the North American calculations to the rest of the world. It is widely thought that land-based contributions of oil and grease are due primarily to vehicle operation and maintenance (Bomboi and Hernández, 1991; Fam et al., 1987; Hoffman and Quinn, 1987a, 1987b; Latimer et al., 1990; Latimer and Quinn, 1998; Zeng and Vista, 1997). Thus, oil and grease loading estimates for the world were based on the number of motor vehicles in different regions of the world as reported by World Resources Institute (1998). Oil and grease loading per vehicle in North America (the United States and Canada) was estimated by using Equations I-4 and I-5.

Equation I-4

$$VEH_{NA} = P_{NA} veh_{NA} = 304{,}078{,}000 \times 0.72$$
$$= 218.936{,}160 veh$$

where $VEHNA$ = number of vehicles in North America,
PNA = population of North America (World Resources Institute, 1998),
$vehNA$ = number of vehicles per capita in North America (World Resources Institute,1998).

Equation I-5

$$l_{NAA} = \frac{L_{NAA}}{VEH_{NA}} = \frac{3{,}443{,}557 \text{ tonne yr}^{-1}}{218{,}936{,}160 \text{ veh}},$$
$$= 0.01573 \text{ tonne veh}^{-1} \text{ yr}^{-1}$$

where $lNAA$ = loading per vehicle in North America based on urban area calculations of total annual load,
$LNAA$ = annual load of land-based contributions of oil and grease in North America based on urban area calculations (from previous calculations; see Table F-9).

The numbers of vehicles in regions of the world were determined by applying Equation I-4 to regional data in World Resources Institute (1998). These numbers of vehicles were then multiplied by the loading per vehicle in North America obtained from Equation I-5 to obtain a world estimate of loading of oil and grease to the sea via land-based contributions. Because data on actual vehicle usage and maintenance in other countries were unavailable, it was assumed that the loadings of oil and grease per vehicle in North America were representative of oil and grease loadings per vehicle in other parts of the world. This assumption was considered reasonable because, while motor vehicles in other countries of the world are not as well maintained as vehicles in North America and therefore would likely contribute more oil and grease per vehicle while running, motor vehicles are less frequently used in other regions of the world.

Calculations for the Coastal Basins of Mexico

Because of a lack of data regarding urban land area for metropolitan areas in Mexico, the following method was used to calculate the land-based contributions of oil and grease to coastal zones H and I:

1. Oil and grease loading from Mexico was estimated using Equation I-4 with population and per capita motor vehicle data from World Resources Institute (1998), and then multiplying by the estimated loading per vehicle for the United States and Canada. These calculations yielded a total oil and grease loading from Mexico of 165,801 tonne yr^{-1}.
2. Metropolitan areas in Mexico with populations of more than 100,000 inhabitants as of 1990 (United Nations, 1998) were partitioned into either coastal zone H or I depending on whether urban drainage from those areas drained to the Gulf of Mexico (zone H) or the Pacific Ocean (zone I). Mexico City and urban areas to the north and east drain to the Grand

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Drainage Canal, eventually flowing to the Gulf of Mexico (National Research Council, 1995b), and were therefore included in coastal zone H. (Contact NRC staff to obtain a listing of the urban areas and corresponding 1990 populations in each coastal zone.)

3. The oil and grease loading calculated in Step 1 was allocated to each coastal zone according to the percentage of the Mexican urban population allocated to that coastal zone. Thus, 65 percent of the total oil and grease loading from Mexico was allocated to coastal zone H, and the rest was allocated to coastal zone I.

Estimates of Petroleum Hydrocarbons and Polycyclic Aromatic Hydrocarbons

The land-based loading calculations of oil and grease described thus far were based on available data from the STORET database that was measured using either the Soxhlet extraction method or liquid-liquid extraction method. These methods determine groups of substances with similar physical characteristics on the basis of their common solubility in a specified solvent (American Society for Testing and Materials, 1999). Thus, "oil and grease" as measured by these methods includes not only petroleum hydrocarbons but also other substances, such as lipid material (American Society for Testing and Materials, 1999; Hoffman and Quinn, 1987a). An investigation was done of published literature to determine if quantifications have been made of the amount of petroleum hydrocarbons or polycyclic aromatic hydrocarbons (PAH) in oil and grease. The literature search revealed a scattering of studies that were generally focused on oil and grease data or specific hydrocarbons, but seldom on total hydrocarbons in oil and grease (Table I-5).

Eganhouse and Kaplan's (1982) study of effluents from wastewater treatment plants in southern California remains the principal study that estimated the proportion of total hydrocarbons in oil and grease. The factor of 0.38 that was applied to oil and grease estimates in the previous National Research Council (1985) report to estimate petroleum hydrocarbon contributions from municipal wastewaters was obtained from the Eganhouse and Kaplan (1982) study. However, wastewater effluent in southern California is not representative of the petroleum hydrocarbon fraction in oil and grease in river water because there are many sources of petroleum hydrocarbons and oil and grease besides municipal wastewaters, the composition of petroleum-derived hydrocarbons varies widely from place to place, and there could be other sources of hydrocarbons such as those produced naturally by aquatic organisms that could be included in oil and grease measurements (Laws, 1993).

New studies were not available that compared concentrations of PAH or total hydrocarbons to oil and grease in water, but Michel (2001) provided data of measured total PAH on the lower Mississippi River in December 2000. These measurements were taken as a result of a spill on the river, but the background measurements of total PAH at three river stations varied from 100 to 156 ng L^{-1}, with an average of 128.3 ng L^{-1}. Using the average oil and grease concentration for the Mississippi River of 0.84 mg L^{-1} from the STORET data (see Table I-2), the estimated percentage of PAH in oil and grease in the Mississippi River would be about 0.015% based on the average total PAH concentration.

PAH typically constitute 0.1-1% of total petroleum hydrocarbons in oil (Wang et al., 1999b). However, since PAH are fairly soluble in water, they likely constitute a larger portion of total petroleum hydrocarbons in oil in water, so the range was expanded to 0.1-10% of total petroleum hydrocarbons, which was verified with comparisons of relative amounts of measured PAH and total hydrocarbons in water in studies in the literature (Table I-6). Thus, estimates of total petroleum hydrocarbons in the Mississippi River based on the December 2000 average PAH data of Michel (2001) would be from 1280 to 128,000 ng L^{-1}. These estimates, when compared to the measured average oil and grease concentrations in the Mississippi River, are 0.15% to 15% of oil and grease, with a best estimate of 1.5%. The best estimate of total hydrocarbon loading from land-based sources was therefore calculated as 1.5% of the best estimate of oil and grease loading.

RESULTS

The average annual loads of oil and grease discharged to the sea were calculated for those rivers with reported oil and grease data in STORET (Table I-7). These total loads were then normalized to unit loads per urban land area. The final estimates of land-based contributions of oil and grease to the sea via all major inland river basins in the United States and Canada were then determined using the 1990s oil and grease data for the Delaware and Mississippi Rivers (Table I-8) with urban land area data from U.S. Bureau of Census (1998) and Statistics Canada (2000). About two-fifths of the estimated loading in North America was determined from actual measured data in STORET, with the remainder determined using the unit load approach.

The estimates of land-based contributions of oil and grease to the sea from both major inland rivers and coastal areas in the United States and Canada were totaled by coastal basin (Table I-9). Table F-9 also shows calculated values for coastal zones in Mexico, but these loads were not included in the totals for North America (i.e., the United States and Canada). The total loading for North America (3.4 million tonne yr^{-1}) was used to obtain a world estimate of land-based oil and grease loading (9.4 million tonne yr^{-1}; Table I-10). The regional distribution of this loading shows that North America and Europe contribute the majority of land-based oil and grease to the sea.

A factor of 0.015 was applied to the total oil and grease loading to estimate the fraction of hydrocarbons in oil and grease. The estimated worldwide loading of hydrocarbons to

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TABLE I-5 Summary of Literature Review for Oil and Grease, Hydrocarbon, and Polycyclic Aromatic Hydrocarbon (PAH) Data Due to Land-based Discharges

Citation	Description
Abdullah et al. (1994)	Hydrocarbons (in oil equivalents) in ocean in Peninsular Malaysia
Abdullah et al. (1996)	Oil and grease and hydrocarbons (in oil equivalents) in ocean in Peninsular Malaysia
Baker (1983)	Synthesis of world hydrocarbon inputs
Bamford et al. (1999a)	PAH in the Patapsco River, an urbanized subestuary of the Chesapeake Bay
Bidleman et al. (1990)	Hydrocarbons in South Carolina estuaries
Bomboi and Hernández (1991)	PAH and hydrocarbons in urban runoff in Madrid, Spain
Burns and Saliot (1986)	Synthesis of hydrocarbon budget for Mediterranean Sea
Carey et al. (1990)	Hydrocarbons and PAH in the Mackenzie River, Canada
Cole et al. (1984)	PAH in urban runoff
Connell (1982)	Hydrocarbon budget for estuary near New York, NY
Cross et al. (1987)	PAH and hydrocarbons in coastal Los Angeles, CA
Crunkilton and DeVita (1997)	PAH in Lincoln Creek, WI
DeLeon et al. (1986)	PAH and hydrocarbons in the Mississippi River
Eganhouse and Kaplan (1981)	Hydrocarbons in urban runoff in southern California
Eganhouse et al. (1981)	Hydrocarbons in urban runoff in southern California
Fam et al. (1987)	PAH and hydrocarbons in urban runoff from watersheds in San Francisco Bay, CA
Frankel (1995)	Synthesis of world oil and grease in industrial discharges
Freedman (1989)	Synthesis of hydrocarbon inputs to world's oceans
Fulton et al. (1993)	PAH in South Carolina estuaries
Gleick (1993)	Synthesis of oil and grease in industrial discharges
Gupta et al. (1981)	Oil and grease in highway runoff at several locations in US; FHWA report
Hall and Anderson (1988)	Hydrocarbons in urban runoff in Burnaby, British Columbia, Canada
Hoffman et al. (1983)	Hydrocarbons in urban runoff in Narragansett Bay, RI
Hoffman et al. (1984)	PAH in urban runoff in RI
Hoffman et al. (1985)	PAH and hydrocarbons in highway runoff in RI
Hoffman and Quinn (1987a, 1987b)	Oil and grease, PAH and hydrocarbons in wastewater treatment plant effluent and urban runoff in combined sewer overflows in RI
Horsfall et al. (1994)	Hydrocarbons in New Calabar River, Nigeria
Hunter et al. (1979)	Hydrocarbons in urban runoff for Philadelphia, PA
Ishaq (1992)	Oil and grease in urban runoff in Riyadh, Saudi Arabia
Ishaq and Alassar (1999)	Oil and grease in urban runoff in Dharan City, Saudi Arabia
Jensen and Jørgensen (1984)	Synthesis of oil and grease and hydrocarbon inputs to the Baltic Sea
Kneip et al. (1982)	Synthesis of oil and grease and hydrocarbons in nonpoint source pollution to New York Bight
Latimer et al. (1990)	PAH and hydrocarbons in urban runoff in Rhode Island
Latimer and Quinn (1998)	Hydrocarbons in dry weather inputs to Narragansett Bay, RI
Laws (1993)	Synthesis of world hydrocarbon inputs
Levins et al. (1979)	Oil and grease in sewage treatment plant effluents at locations in US; EPA report
Lopes and Dionne (1998)	Synthesis of oil and grease, PAH, and hydrocarbons in highway runoff and urban stormwater
MacKenzie and Hunter (1979)	PAH and hydrocarbons in urban runoff for Philadelphia, PA
Makepeace et al. (1995)	Synthesis of oil and grease and hydrocarbons in urban runoff
Mastran et al. (1994)	PAH in Occoquan Reservoir, VA due to boating activity
McCarthy et al. (1997)	PAH in Slave River, Canada
McFall et al. (1985)	PAH in water column of Lake Pontchartrain, LA
Michael (1982)	Synthesis of oil and grease and hydrocarbon inputs to New York Bight
NOAA (1987)	Oil and grease, PAH and hydrocarbon inputs to Narragansett Bay, RI
NRC (1985)	Synthesis of world oil and grease and hydrocarbon inputs to the ocean
Odokuma and Okpokwasili (1997)	Oil and grease in New Calabar River, Nigeria
OTA (1987)	Synthesis of oil and grease contributions to coastal waters in US
Owe et al. (1982)	Hydrocarbons in urban runoff for Syracuse, NY
Perry and McIntyre (1986)	Oil and grease and PAH in highway runoff near London, UK
Perry and McIntyre (1987)	Oil and grease and PAH in highway runoff near London, UK
Petty et al. (1998)	PAH in Missouri River following flood of 1993
Pham and Proulx (1997)	PAH in Montreal wastewater and St. Lawrence River
Pham et al. (1999)	PAH in Montreal wastewater and St. Lawrence River
Rifai et al. (1993)	Oil and grease inputs to Galveston Bay, TX
Roesner (1982)	Synthesis of oil and grease in urban runoff at various locations in US
Rogers (1994)	Synthesis of oil and grease in combined sewer overflows and urban runoff
Schiff and Stevenson (1996)	Oil and grease in urban runoff in San Diego, CA

continued

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TABLE I-5 Continued

Citation	Description
Shaheen (1975)	Oil and grease in dust in Washington, DC area; EPA report
Stenstrom et al. (1984)	Oil and grease in urban runoff in Richmond, CA
Stenstrom et al. (1987)	Oil and grease and PAH in urban runoff in the San Francisco Bay Area, CA
Telang et al. (1981)	Hydrocarbons in the Marmot Basin, Alberta, Canada
Tomlinson et al. (1980)	Oil and grease in combined sewer overflows, storm drains in Seattle, WA; EPA rpt
USEPA (1996)	Synthesis of impaired rivers and streams due to oil and grease pollution
USEPA (1998)	Synthesis of impaired estuaries due to oil and grease pollution
USEPA (1999)	Synthesis of oil and grease in industrial discharges in US
Wakeham (1977)	Hydrocarbon budget for Lake Washington, WA
Walker et al. (1999)	PAH in urban runoff to Passaic River, NJ
Whipple and Hunter (1979)	Hydrocarbons in urban runoff to the Delaware estuary
Yamane et al. (1990)	Hydrocarbons and PAH in stormwater runoff in Tama River Basin, Tokyo, Japan
Yunker and MacDonald (1995)	PAH in the Mackenzie River, Canada
Yunker et al. (1991)	PAH in the Mackenzie River, Canada
Zeng and Vista (1997)	PAH near San Diego, CA

NOTES: NOAA = National Oceanic and Atmospheric Administration; NRC = National Research Council; OTA = Office of Technology Assessment; USEPA = U.S. Environmental Protection Agency

TABLE I-6 Comparisons of PAH and Total Hydrocarbon Concentrations in Water in Literature

Reference	Description	Total PAH or Aromatics (ng L^{-1})	Total Hydrocarbons (TH) (ng L^{-1})	Ratio of PAH:TH
Bomboi and Hernández (1991)	Urban runoff in Madrid, Spain	27,800	1,181,800	0.0235
DeLeon et al. (1986)	Mississippi River	79	435	0.1816
Eganhouse and Kaplan (1981)	Los Angeles River storm runoff (est.)	1,600,000	13,100,000	0.1221
Hunter et al. (1979)	Philadelphia urban runoff	1,120,000	3,690,000	0.3035
Maldonado et al. (1999)	Black Sea	0.045–2.219	1.61–100	0.00045–0.0279

TABLE I-7 Calculated Annual and Unit Loads of Oil and Grease for Major Inland Rivers in North America with STORET Data

River	Land Area[a] (m^2)	Population[b]	Average Annual Load (tonne yr^{-1})	Unit Load per Urban Land Area (g m^{-2} yr^{-1})
Columbia	30,466,548,140	1,263,460	397,606	13.05
Delaware	5,082,592,668	967,893	62,646	12.33
Delaware (1990s)	5,082,592,668	967,893	62,130	12.22
Hudson	21,972,423,133	1,432,124	748,083	34.05
James	7,686,825,713	354,043	119,834	15.59
Mississippi	463,617,454,706	40,383,189	934,579	2.02
Mississippi (1990s)	463,617,454,706	40,383,189	525,638	1.13
Neuse	10,472,875,923	1,162,035	0	0
Sabine	6,964,737,028	374,973	17,608	2.53
Sacramento	30,438,835,267	2,152,519	17,430	0.57
Susquehanna	27,400,261,216	2,788,354	0	0
Trinity	23,581,064,748	4,683,013	73,162	3.10

NOTES: [a]Source: U.S. Bureau of the Census (1998), Table B-1; includes dry land and land temporarily or partially covered by water; [b]Source: U.S. Bureau of the Census (1998), Table B-1; based on areas defined as of June 30, 1996.

the sea from land-based sources was therefore 141,000 tonne yr^{-1} (Table I-11).

A factor of 0.00015 was applied to the total oil and grease loading to estimate the fraction of PAH in oil and grease. The estimated worldwide loading of PAH to the sea from land-based sources was therefore 1,400 tonne yr^{-1} (Table I-11).

Discussion

The method used to estimate land-based oil and grease, hydrocarbon, and PAH contributions to the sea involved a large degree of uncertainty due to a number of factors, including (but not limited to):

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TABLE I-8 Final Estimates of Land-based Contributions of Oil and Grease to the Sea via Major Inland River Basins in North America

River	No. of Observations	Avg. Conc. Oil & Grease, Ci (mg L^{-1})	Average Annual Flow, Qi (m^3 yr^{-1})	Urban Land Area in Watershed, Aui (m^2)	Annual Load, Lai (tonne yr^{-1})	Unit Load per Urban Land Area, Lai (g m^{-2} yr^{-1})[a]
Calculated from STORET data						
Delaware (1990s)	99	5.80[b]	10.7×10^9	5.1×10^9	62,130	12.22
Mississippi (1990s)	46	0.84[b]	625.8×10^9	463.6×10^9	525,638	1.13
Subtotal				468.7×10^9	587,768	
Calculated using alternative method						
Alabama-Tombigbee				19.8×10^9	24,890	1.25
Altamaha				5.5×10^9	6,896	1.25
Apalachicola				21.7×10^9	27,223	1.25
Brazos				14.4×10^9	18,039	1.25
Colorado (TX)				14.9×10^9	18,670	1.25
Columbia				30.5×10^9	38,206	1.25
Copper				0	0	0
Hudson				22.0×10^9	268,593	12.22
James				7.7×10^9	93,964	12.22
Neuse				10.5×10^9	13,133	1.25
Potomac				2.0×10^9	2,446	1.25
Rio Grande				43.8×10^9	54,982	1.25
Roanoke				4.8×10^9	6,057	1.25
Sabine				7.0×10^9	8,734	1.25
Sacramento				30.4×10^9	38,171	1.25
St. Lawrence				19.7×10^9	24,699	1.25
San Joaquin				46.0×10^9	57,647	1.25
Santee				26.8×10^9	33,573	1.25
Saskatchewan				34.7×10^9	43,542	1.25
Savannah				6.3×10^9	7,954	1.25
Susitna				0	0	0
Susquehanna				27.4×10^9	34,361	1.25
Trinity				23.6×10^9	29,572	1.25
Yukon				0	0	0
Subtotal				419.4×10^9	851,352	
Average						2.68
Total				888.1×10^9	1,439,352	

NOTES: [a]Unit loads shown for alternate method rivers are those used to calculate annual load; [b]freon-gr method used to measure oil and grease concentrations.

TABLE I-9 Final Estimates of Land-based Contributions of Oil and Grease to the Sea by Coastal Zones in North America and Mexico

Coastal Zone	Description	Urban Population in Watershed, Pi (1997)	Urban Land Area in Watershed, Aui (m^2)	Annual Load, Lai (tonne yr^{-1})	Unit Load per Urban Land Area, Lai (g m^{-2} yr^{-1})[a]
A	No urban areas	0	0	0	0
B	Coastal	0	0	0	0
	Saskatchewan	293.1×10^3	34.7×10^9	43,542	1.25
	Subtotal	293.1×10^3	34.7×10^9	43,542	
C	Coastal	632.3×10^3	6.8×10^9	8,529	1.25
	St. Lawrence	$5,647.8\times10^3$	19.7×10^9	24,699	1.25
	Subtotal	$6,280.1\times10^3$	26.5×10^9	33,228	
D	Coastal	$44,843.3\times10^3$	121.7×10^9	1,487,571	12.22
	Delaware	967.9×10^3	5.1×10^9	62,130	12.22
	Hudson	$1,432.1\times10^3$	22.0×10^9	268,593	12.22
	James	354.0×10^3	7.7×10^9	93,964	12.22
	Potomac	99.1×10^3	2.0×10^9	2,446	1.25
	Susquehanna	$2,788.4\times10^3$	27.4×10^9	34,361	1.25
	Subtotal	$50,484.8\times10^3$	185.8×10^9	1,949,065	

continues

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TABLE I-9 Continued

Coastal Zone	Description	Urban Population in Watershed, Pi (1997)	Urban Land Area in Watershed, Aui (m^2)	Annual Load, Lai (tonne yr^{-1})	Unit Load per Urban Land Area, Lai (g m^{-2} yr^{-1})[a]
E	Coastal	$11,839.8\times10^3$	79.8×10^9	100,104	1.25
	Altamaha	454.6×10^3	5.5×10^9	6,896	1.25
	Neuse	$1,162.0\times10^3$	10.5×10^9	13,133	1.25
	Roanoke	337.1×10^3	4.8×10^9	6,057	1.25
	Santee	$3,198.3\times10^3$	26.8×10^9	33,573	1.25
	Savannah	457.2×10^3	6.3×10^9	7,954	1.25
	Subtotal	$17,449.2\times10^3$	133.7×10^9	167,717	
F	Coastal	$5,355.1\times10^3$	42.3×10^9	53,108	1.25
	Alabama-Tombigbee	$1,601.4\times10^3$	19.8×10^9	24,890	1.25
	Apalachicola	$4,016.9\times10^3$	21.7×10^9	27,223	1.25
	Subtotal	$10,973.3\times10^3$	83.9×10^9	105,222	
G	Coastal	$10,127.3\times10^3$	75.3×10^9	94,398	1.25
	Gulf coast refineries[b]	—	—	2,882	—
	Brazos	987.8×10^3	14.4×10^9	18,039	1.25
	Colorado (TX)	$1,173.7\times10^3$	14.9×10^9	18,670	1.25
	Mississippi	$40,383.2\times10^3$	463.6×10^9	525,638	1.13
	Rio Grande	$1,410.0\times10^3$	43.8×10^9	54,982	1.25
	Sabine	375.0×10^3	7.0×10^9	8,734	1.25
	Trinity	$4,683.0\times10^3$	23.6×10^9	29,572	1.25
	Subtotal	$59,139.9\times10^3$	642.6×10^9	752,913	
H[c]	Coastal and inland rivers	$30,159.2\times10^3$		108,189	
I	No urban areas	0	0	0	0
J[c]	Coastal and inland rivers	$16,060.2\times10^3$	57,612		
K	Coastal	$18,331.5\times10^3$	98.9×10^9	123,976	1.25
L	Coastal	$7,686.2\times10^3$	43.3×10^9	54,349	1.25
	Sacramento	$2,152.5\times10^3$	30.4×10^9	38,171	1.25
	San Joaquin	$2,382.3\times10^3$	46.0×10^9	57,647	1.25
	Subtotal	$12,221.1\times10^3$	119.7×10^9	150,168	
M	Coastal	$5,946.3\times10^3$	54.0×10^9	67,725	1.25
	Columbia	$1,263.5\times10^3$	30.5×10^9	38,206	1.25
	Subtotal	$7,209.7\times10^3$	84.5×10^9	105,931	
N	Coastal	$2,136.0\times10^3$	3.5×10^9	4,332	1.25
O	Coastal	869.9×10^3	1.6×10^9	1,949	1.25
P	Coastal	251.0×10^3	4.4×10^9	5,514	1.25
	Copper	0	0	0	0
	Susitna	0	0	0	0
	Subtotal	251.0×10^3	4.4×10^9	5,514	
Q	Coastal	0	0	0	0
	Yukon	0	0	0	0
	Total[c]	$188,277.0\times10^3$	$1,419.7\times10^9$	3,443,557	

NOTES: [a]Unit loads shown are those used to calculate corresponding annual load; [b]See Table I-4 for calculation of refinery loading; [c]Total does not include Coastal Zones in Mexico.

TABLE I-10 World Estimates of Land-based Sources of Oil and Grease to the Sea

Region	Population (WRI 1998)	Motor Vehicles Per Capita (WRI 1998)	Number of Vehicles	Loading per Vehicle (tonne veh^{-1})	Loading (tonne yr^{-1})
Africa	778,484,000	0.02	15,569,680	0.01573	244,889
Europe	729,406,000	0.27	196,939,620	0.01573	3,097,582
North America	304,078,000	0.72	218,936,160	0.01573	3,443,557
Central America	130,710,000	0.11	14,378,100	0.01573	226,147
South America	331,889,000	0.09	29,870,010	0.01573	469,813
Asia	3,588,877,000	0.03	107,666,310	0.01573	1,693,439
Oceania	29,460,000	0.43	12,667,800	0.01573	199,247
Total					9,374,674

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TABLE I-11 Final Estimates of Worldwide Land-based Contributions of Hydrocarbons and Polycyclic Aromatic Hydrocarbons (PAH) to the Sea

World Region	Coastal Zone	Description	Hydrocarbons (tonne yr^{-1})	PAH (tonne yr^{-1})
North America[a]	A	No urban areas	0	0
	B	Coastal	0	0
		Saskatchewan	653	7
		Subtotal	653	7
	C	Coastal	128	1
		St. Lawrence	370	4
		Subtotal	498	5
	D	Coastal	22,314	223
		Delaware	932	9
		Hudson	4,029	40
		James	1,409	14
		Potomac	37	0
		Susquehanna	515	5
		Subtotal	29,236	292
	E	Coastal	1,502	15
		Altamaha	103	1
		Neuse	197	2
		Roanoke	91	1
		Santee	504	5
		Savannah	119	1
		Subtotal	2,516	25
	F	Coastal	797	8
		Alabama-Tombigbee	373	4
		Apalachicola	408	4
		Subtotal	1,578	16
	G	Coastal	1,416	14
		Gulf coast refineries[b]	43	0
		Brazos	271	3
		Colorado (TX)	280	3
		Mississippi	7,885	79
		Rio Grande	825	8
		Sabine	131	1
		Trinity	444	4
		Subtotal	11,294	113
	H[a]	Coastal and inland rivers	1,623	16
	I[a]	No urban areas	0	0
	J	Coastal and inland rivers	864	9
	K	Coastal	1,860	19
	L	Coastal	815	8
		Sacramento	573	6
		San Joaquin	865	9
		Subtotal	2,253	23
	M	Coastal	1,016	10
		Columbia	573	6
		Subtotal	1,589	16
	N	Coastal	65	1
	O	Coastal	29	0
	P	Coastal	83	1
		Copper	0	0
		Susitna	0	0
		Subtotal	83	1
	Q	Coastal	0	0
		Yukon	0	0
		Subtotal[a]	51,653	517
Africa			3,673	37
Europe			46,464	465
Central America			3,392	34
South America			7,047	70
Asia			25,402	254
Oceania			2,989	30
TOTAL			140,620	1,406

NOTES: [a]Subtotal for North America does not include Coastal Zones in Mexico; [b]See Table I-4 for calculation of refinery loading.

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- Lack of data; only nine major rivers in the United States had oil and grease data in the U.S. Environmental Protection Agency's STORET data base, and several of these consisted of very few observations.
- Differences in measuring and reporting data; most of the available oil and grease data in STORET was gathered using either the Soxhlet extraction method or the liquid-liquid extraction method. The minimum detection limit (denoted off-scale low in the STORET records) and approach for reporting values measured below the detection limit varied with location and time. For example, the minimum detection limit on the Delaware River was 2 mg L^{-1} for data reported from 1988-1994, and 5 mg L^{-1} for data reported after 1994. By comparison, the minimum detection limit on the Mississippi River was 1 mg L^{-1} for the entire period of record (1973-1996).
- Adjustment of off-scale low measurements; these values were set to half their reported value even though the actual value was unknown.
- Estimating the proportion of petroleum-related hydrocarbons and PAH in oil and grease measurements

Quantifying the uncertainty in the estimates presented in this analysis was not possible, but a reasonable estimate of the low and high ranges of the calculated oil and grease values was made by assuming that the data available from the 1990s for the Mississippi and Delaware rivers, respectively, represented the low and high bounds of oil and grease unit loading for the rivers for which STORET data were unavailable in the 1990s, and for coastal zones in North America and the world (Table I-12). Based on these assumptions, the range of worldwide loadings of land-based sources of oil and grease to the sea was 4.5 million–33.3 million tonne yr^{-1}, with a best estimate of 9.4 million tonne yr^{-1}. The values shown in Table I-12 also reflect low, best, and high estimates of oil and grease loadings from Gulf coast refineries. Calculations of oil and grease discharges using daily maximum guidelines (6.0 lbs per 1000 barrels of crude produced) were used as a high estimate of these loadings, while calculations using the monthly average guidelines (3.2 lbs per 1000 barrels of crude produced) were used as a low estimate. The average of the two calculations was used as a best estimate of the loadings.

Estimates of total petroleum hydrocarbons in the Mississippi River were based on the December 2000 average PAH data of Michel (2001), the assumption that PAH constitute 0.1%–10% of total petroleum hydrocarbons, and the 1990s' measured average oil and grease concentration of 0.84 mg L^{-1}. Thus, using the lower bound of PAH fraction in total hydrocarbons, a lower bound for estimated hydrocarbons in oil and grease was 0.15%, while an upper bound of hydrocarbons as 15% of oil and grease was determined assuming PAH constitute 10% of total petroleum hydrocarbons. The final range of estimates of total hydrocarbons were therefore made by assuming that the low estimate corresponded with the low percentage of total hydrocarbons (i.e., 0.15%) in the low estimate of oil and grease loading, the best estimate corresponded with 1.5% of total hydrocarbons in the best estimate of oil and grease loading, and the high estimate corresponded with the high percentage of total hydrocarbons (i.e., 15%) in the high estimate of oil and grease loading (Table I-13). Thus, the range of land-based petroleum hydrocarbon loading to the sea was 6,800–5,000,000 tonne yr^{-1}, with a best estimate of 141,000 tonne yr^{-1}.

The application of the PAH data of Michel (2001) on the Mississippi River involved uncertainties regarding the degree to which that data were representative of distributions of PAH in land-based discharges to the sea via rivers and coastal discharges. Part of this uncertainty arises from the lack of consistent PAH measurements in the water column. A review of STORET and the USGS' National Water Information Service (NWIS) data revealed less than a dozen measurements of PAH above detection limits on rivers in the United States. Furthermore, reported water column PAH concentrations in the literature were not consistent with respect to the constituents reported, did not use the same measurement methods, and/or did not include particulate and dissolved concentrations of PAH. Nonetheless, literature-reported data and data provided by Baker (2001) on the Susquehanna River indicated that the Michel (2001) data were within a reasonable range for river total PAH concentrations. Thus, the range of the background measurements of total PAH on the Mississippi River by Michel (2001) (i.e., 100 to 156 ng L^{-1}, with an average of 128.3 ng L^{-1}) were compared with the average oil and grease concentration for the Mississippi River of 0.84 mg L^{-1} to determine the estimated range of PAH in oil and grease as 0.012% to 0.019%, with a best estimate of 0.015%. The low estimate of PAH loading to the sea from land-based sources was therefore estimated as 0.012% of the low estimate of oil and grease loading, and the high PAH loading estimate was calculated as 0.019% of the high estimate of oil and grease loading. The best estimate of PAH loading from land-based sources was calculated using 0.015% of the best estimate of oil and grease loading (Table I-13). The range of PAH loading to the sea from land-based sources was 500–6,300 tonne yr^{-1}, with a best estimate of 1,400 tonne yr^{-1}.

Comparison of Estimates of Land-Based Loading with Other Estimates

The average oil and grease loading of 2.68 g m^{-2} yr^{-1} estimated in this study (see Table I-8) was comparable to oil and grease loadings estimated for urban areas in other studies (Table I-14). The range of estimates presented in the current analysis (1.13–12.22 g m^{-2} yr^{-1}) encompassed the estimates of the previous studies. Perry and McIntyre's (1986) estimate was actually an event-based calculation that should be higher than an annual load. In addition, the estimates by

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TABLE I-12 Ranges of Worldwide Land-based Contributions of Oil and Grease to the Sea

			Unit Load Based on Urban Area ($g\ m^{-2}\ yr^{-1}$)			Annual Load ($tonne\ yr^{-1}$)		
World Region	Coastal Zone	Description	Low	Best Est.	High	Low	Best Est.	High
North America[a]	A	No urban areas	0	0	0	0	0	0
	B	Coastal	0	0	0	0	0	0
		Saskatchewan	1.13	1.25	12.22	39,367	43,542	424,440
		Subtotal				39,367	43,542	424,440
	C	Coastal	1.13	1.25	12.22	7,711	8,529	82,137
		St. Lawrence	1.13	1.25	12.22	22,330	24,699	240,759
		Subtotal				30,041	33,228	323,896
	D	Coastal	1.13	12.22	12.22	137,971	1,487,571	1,487,571
		Delaware	12.22	12.22	12.22	62,130	62,130	62,130
		Hudson	1.13	12.22	12.22	24,912	268,593	268,593
		James	1.13	12.22	12.22	8,715	93,964	93,964
		Potomac	1.13	1.25	12.22	2,211	2,446	23,843
		Susquehanna	1.13	1.25	12.22	31,066	34,361	334,943
		Subtotal				267,005	1,949,065	2,271,044
	E	Coastal	1.13	1.25	12.22	90,504	100,104	975,790
		Altamaha	1.13	1.25	12.22	6,234	6,896	67,218
		Neuse	1.13	1.25	12.22	11,874	13,133	128,021
		Roanoke	1.13	1.25	12.22	5,476	6,057	59,043
		Santee	1.13	1.25	12.22	30,353	33,573	327,262
		Savannah	1.13	1.25	12.22	7,191	7,954	77,533
		Subtotal				151,633	167,717	1,634,867
	F	Coastal	1.13	1.25	12.22	48,015	53,108	517,689
		Alabama-Tombigbee	1.13	1.25	12.22	22,503	24,890	242,625
		Apalachicola	1.13	1.25	12.22	24,613	27,223	265,366
		Subtotal				95,131	105,222	1,025,680
	G	Coastal	1.13	1.25	12.22	85,345	94,398	920,166
		Gulf coast refineries	—	—	—	2,005	2,882	3,759
		Brazos	1.13	1.25	12.22	16,309	18,039	175,838
		Colorado (TX)	1.13	1.25	12.22	16,879	18,670	181,989
		Mississippi	1.13	1.13	1.13	525,638	525,638	525,638
		Rio Grande	1.13	1.25	12.22	49,709	54,982	535,947
		Sabine	1.13	1.25	12.22	7,896	8,734	85,137
		Trinity	1.13	1.25	12.22	26,736	29,572	288,257
		Subtotal				730,517	752,913	2,716,731
	H*a*	Coastal and inland rivers				52,405	108,189	383,817
	I	No urban areas	0	0	0	0	0	0
	J[a]	Coastal and inland rivers				27,906	57,612	204,387
	K	Coastal	1.13	1.25	12.22	112,086	123,976	1,208,486
	L	Coastal	1.13	1.25	12.22	49,137	54,349	529,786
		Sacramento	1.13	1.25	12.22	34,511	38,171	372,087
		San Joaquin	1.13	1.25	12.22	52,118	57,647	561,928
		Subtotal				135,767	150,168	1,463,800
	M	Coastal	1.13	1.25	12.22	61,230	67,725	660,166
		Columbia	1.13	1.25	12.22	34,542	38,206	372,425
		Subtotal				95,772	105,931	1,032,591
	N	Coastal	1.13	1.25	12.22	3,916	4,332	42,223
	O	Coastal	1.13	1.25	12.22	1,762	1,949	19,002
	P	Coastal	1.13	1.25	12.22	4,985	5,514	53,746
		Copper	0	0	0	0	0	0
		Susitna	0	0	0	0	0	0
		Subtotal				4,985	5,514	53,746
	Q	Coastal	0	0	0	0	0	0
		Yukon	0	0	0	0	0	0
		Subtotal[a]				1,667,983	3,443,557	12,216,509
Africa						118,619	244,889	868,779
Europe						1,500,400	3,097,582	10,989,115
Central America						109,541	226,147	802,290
South America						227,567	469,813	1,666,729
Asia						820,264	1,693,439	6,007,717
Oceania						96,511	199,247	706,856
TOTAL						4,540,885	9,374,674	33,257,994

NOTES: [a]Subtotal for North America does not include Coastal Zones in Mexico.

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TABLE I-13 Ranges of Worldwide Land-based Contributions of Hydrocarbons and Polycyclic Aromatic Hydrocarbons (PAH) to the Sea

			Hydrocarbons (tonne yr^{-1})			PAH (tonne yr^{-1})		
World Region	Coastal Zone	Description	Low	Best Est.	High	Low	Best Est.	High
North America[a]	A	No urban areas	0	0	0	0	0	0
	B	Coastal	0	0	0	0	0	0
		Saskatchewan	59	653	63,666	5	7	81
		Subtotal	59	653	63,666	5	7	81
	C	Coastal	12	128	12,471	1	1	16
		St. Lawrence	33	370	36,114	3	4	46
		Subtotal	45	498	48,584	4	5	62
	D	Coastal	207	22,314	223,136	17	223	283
		Delaware	93	932	9,320	7	9	12
		Hudson	37	4,029	40,289	3	40	51
		James	13	1,409	14,095	1	14	18
		Potomac	3	37	3,576	0	0	5
		Susquehanna	47	515	50,241	4	5	64
		Subtotal	401	29,236	340,657	32	292	431
	E	Coastal	136	1,502	149,368	11	15	185
		Altamaha	9	103	10,083	1	1	13
		Neuse	18	197	19,203	1	2	24
		Roanoke	8	91	8,856	1	1	11
		Santee	46	504	49,089	4	5	62
		Savannah	11	119	11,630	1	1	15
		Subtotal	227	2,516	245,230	18	25	311
	F	Coastal	72	797	77,653	6	8	98
		Alabama-Tombigbee	34	373	36,394	3	4	46
		Apalachicola	37	408	39,805	3	4	50
		Subtotal	143	1,578	153,852	11	16	195
	G	Coastal	128	1,416	138,025	10	14	175
		Gulf coast refineries	3	43	564	0	0	1
		Brazos	24	271	26,376	2	3	33
		Colorado (TX)	25	280	27,298	2	3	35
		Mississippi	788	7,885	78,846	63	79	100
		Rio Grande	75	825	80,392	6	8	102
		Sabine	12	131	12,771	1	1	16
		Trinity	40	444	43,239	3	4	55
		Subtotal	1,096	11,294	407,510	88	113	516
	H[a]	Coastal and inland rivers	79	1,623	57,573	6	16	73
	I	No urban areas	0	0	0	0	0	0
	J[a]	Coastal and inland rivers	42	864	30,658	3	9	39
	K	Coastal	168	1,860	181,273	13	19	230
	L	Coastal	74	815	79,468	6	8	101
		Sacramento	52	573	55,813	4	6	71
		San Joaquin	78	865	84,289	6	9	107
		Subtotal	204	2,253	219,570	16	23	278
	M	Coastal	92	1,016	99,025	7	10	125
		Columbia	52	573	55,864	4	6	71
		Subtotal	144	1,589	159,889	11	16	196
	N	Coastal	6	65	6,333	0	1	8
	O	Coastal	3	29	2,850	0	0	4
	P	Coastal	7	83	8,062	1	1	10
		Copper	0	0	0	0	0	0
		Susitna	0	0	0	0	0	0
		Subtotal	7	83	8,062	1	1	10
	Q	Coastal	0	0	0	0	0	0
		Yukon	0	0	0	0	0	0
		Subtotal[a]	2,502	51,653	1,832,476	200	517	2,321
Africa			178	3,673	130,317	14	37	165
Europe			2,251	46,464	1,648,387	180	465	2,088
Central America			164	3,392	120,343	13	34	152
South America			341	7,047	250,009	27	70	317
Asia			1,230	25,402	901,158	98	254	1,141
Oceania			145	2,989	106,028	12	30	134
TOTAL			6,811	140,620	4,988,699	545	1,406	6,319

NOTES: [a]Subtotal for North America does not include Coastal Zones in Mexico.

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TABLE I-14 Comparison of Estimated Loading of Oil and Grease in Urban Areas

Location	Unit Load per Urban Land Area ($g\ m^{-2}\ yr^{-1}$)	Reference	Comments
United States and Canada	2.68	This work	
Los Angeles River, Calif.	1.28	Eganhouse and Kaplan (1981)	Total hydrocarbons
Narragansett Bay, R. I.	2.13	Hoffman et al. (1983)	Petroleum hydrocarbons
United Kingdom (roadway runoff)	11.016	Perry and McIntyre (1986)	Calculated from oil mass loading of 0.17 kg ha^{-1} mm of $runoff^{-1}$ and annual average rainfall of 648 mm
Richmond, Calif.	1.25	Stenstrom et al. (1984)	

Hoffman et al. (1983) and Eganhouse and Kaplan (1981) were actually for hydrocarbons, which constitute part, but not all, of oil and grease. Thus, the lower loadings calculated in those studies agree nicely with the loading estimate from the current study.

The estimate of total oil and grease loading was also compared with estimates of dissolved organic carbon (DOC) inputs to the sea from land-based sources (Table I-15). Since oil and grease constitutes a small part of DOC, the current estimates of oil and grease loading should be considerably lower than estimates of DOC flux. This was confirmed for published estimates of global contributions of DOC from rivers to oceans, although the current estimates of oil and grease loading were higher on the Delaware River than corresponding published estimates of DOC flux by Leenheer (1982).

The current study's best estimates of oil and grease loadings to coastal zone G were on the order of 800,000 tonne yr^{-1}, which was much greater than the 27,000 tonne yr^{-1} estimated by the Caribbean Environment Programme (1994) for the Gulf coast of the United States. It is likely that the Caribbean Environment Programme (1994) data included neither the Mississippi River, which accounted for over 500,000 tonne yr^{-1} of the oil and grease loading in the current study, nor the contributions from Gulf coast refineries. Thus, the corresponding current best estimate was about 10 times greater than the Caribbean Environment Programme (1994) estimate of loading of oil and grease to the Gulf coast.

The calculations of oil and grease loadings presented in this analysis were based on unit loadings per urban land area. Comparison calculations were also made based on unit loadings per capita urban population using 1997 urban populations in the United States obtained from U.S. Bureau of the Census (1998) and 1996 urban populations in Canada from Statistics Canada (2000). These calculations resulted in oil and grease loadings of the same magnitude as calculations based on unit loadings per urban land area (Table I-16).

To test the assumption that the measured oil and grease concentrations used for the current analysis were representative of ambient concentrations in North American rivers, average measured oil and grease concentrations for the 1990s STORET data on the Mississippi and Delaware rivers were compared with a database consisting of all of the 1990s oil and grease measurements gathered from STORET (145 data points) and 704 additional data points from USGS sampling stations on rivers in Louisiana in the 1990s (Table I-17 and Figure I-1). For the Mississippi River and Louisiana sampling, the minimum detection limit was 1 mg L^{-1}, while the minimum detection limit on the Delaware River was either 2 mg L^{-1} or 5 mg L^{-1}. Measurements reported to be less than the minimum detection limit were assumed to be half of their reported value (i.e., if a measurement was reported as <1 mg L^{-1}, 0.5 mg L^{-1} was entered in the database).

The comparisons shown in Table I-17 and Figure I-1 indicate that the oil and grease concentrations used for the Mississippi River in this analysis corresponded nicely with the separate measurements in Louisiana by the USGS and hence the overall database. This result was not surprising since a large portion of the Louisiana data were also measured on the Mississippi River. The Delaware River concentrations were higher than the other 1990s data collected, but the high industrialization of that river could account for higher oil and grease discharges. Thus, the oil and grease concentrations obtained from the STORET database were reasonable.

As a further test of the reasonableness of the estimates of land-based loadings of oil and grease presented here, these loads were compared to oil consumption. According to a recent BP Amoco report (BP Amoco, 2000), North America consumed 1047.1 million tonnes of oil in 1999. Assuming that all of the 3.4 million tonne yr^{-1} of oil and grease estimated in this study as returning to the sea from land-based sources were petroleum-derived, then only about 0.3 percent of consumed oil was returned to the sea from land-based sources. Furthermore, BP Amoco (2000) estimated that the North American annual consumption of oil was broken down as follows:

Gasoline	428.8 million tonne yr^{-1}
Middle Distillates	319.6
Fuel Oil	77.3
Other	221.4
Total	1047.1 million tonne yr^{-1}

Again, assuming that (1) all gasoline products were completely consumed by use (although PAH in urban runoff are

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TABLE I-15 Comparison of Published Estimates of Dissolved Organic Carbon (DOC) Inputs from Land-based Sources to Oil and Grease Loadings Estimated in this Study

Reference	Description	Estimated DOC Flux (tonne C yr^{-1})	Estimated Oil and Grease Loading (tonne yr^{-1})	Percent of DOC Flux
Degens and Ittekkot (1983)	DOC transported by rivers into ocean	285,000,000	9,374,674	3.29
Degens et al. (1991)	DOC flux from Africa	24,700,000	244,889	0.10
Degens et al. (1991)	DOC flux from Asia	94,000,000	1,693,439	1.80
Degens et al. (1991)	DOC flux from North America	33,800,000	3,443,557	10.19
Degens et al. (1991)	DOC flux from South America	44,200,000	469,813	1.06
Kobak (1988)[a]	Inflow of organic matter with river runoff	210,000,000	9,374,674	4.46
Leenheer (1982)	DOC flux from Alabama-Tombigbee	537,000	24,890	4.64
Leenheer (1982)	DOC flux from Apalachicola	136,000	27,223	20.02
Leenheer (1982)	DOC flux from Columbia	1,346,000	38,206	2.84
Leenheer (1982)	DOC flux from Delaware	50,000	62,130	124.26
Leenheer (1982)	DOC flux from Mississippi	3,477,000	525,638	15.12
Leenheer (1982)	DOC flux from Potomac	1,070,000	2,446	0.23
Leenheer (1982)	DOC flux from Sacramento	77,000	38,171	49.57
Leenheer (1982)	DOC flux from Susitna	231,000	0	0.00
Leenheer (1982)	DOC flux from Susquehanna	225,000	34,361	15.27
Leenheer (1982)	DOC flux from Yukon	2,411,000	0	0.00
Leenheer (1982)[b]	DOC flux from United States	10,156,000	3,443,557	33.91
Meybeck (1988)[c]	DOC export as estimated by morphoclimatic zones	234,200,000	9,374,674	4.00
Pocklington and Tan (1983)	DOC flux from St. Lawrence	1,710,000	24,699	1.44
Schlesinger (1997)	Riverine flux of dissolved organic carbon	400,000,000	9,374,674	2.34
Siegenthaler and Sarmiento (1993)[d]	River inputs	800,000,000	9,374,674	1.17
Spitzy and Ittekkot (1991)	Global riverine DOC flux	218,000,000	9,374,674	4.30

NOTES: [a]As cited in Kagan (1995); [b]Leenheer (1982) calculation is for US only; calculations in this work are for North America; [c]As cited in Spitzy and Ittekkot (1991); [d]As cited in McCarthy (2000).

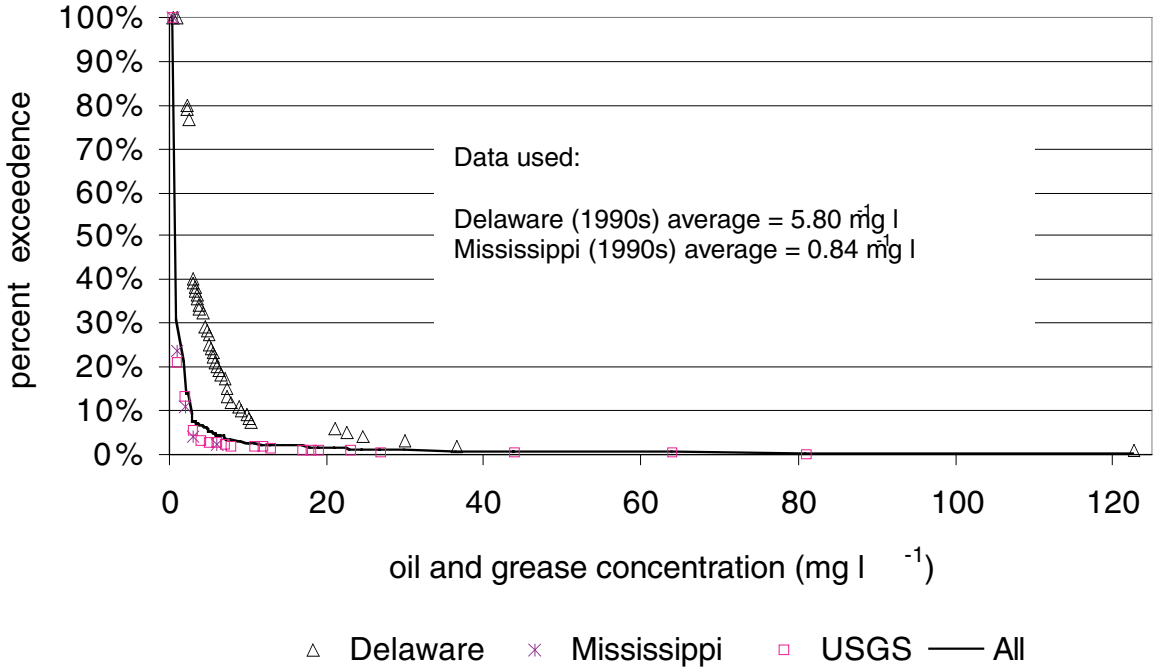

FIGURE I-1 Plot of percent exceedence values for 1990s STORET data (Delaware and Mississippi Rivers), 1990s USGS Louisiana data, and all data combined.

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TABLE I-16 Comparison of Estimates of Worldwide Land-based Contributions of Oil and Grease to the Sea Based on Unit Loads per Urban Land Area and Unit Loads per Capita Urban Population

World Region	Coastal Zone	Description	Annual Load Based on Pop. (tonne yr^{-1})	Annual Load Based on Area (tonne yr^{-1})
North America[a]	A	No urban areas	0	0
	B	Coastal	0	0
		Saskatchewan	41,655	43,542
		Subtotal	41,655	43,542
	C	Coastal	8,987	8,529
		St. Lawrence	80,278	24,699
		Subtotal	89,265	33,228
	D	Coastal	2,878,535	1,487,571
		Delaware	62,130	62,130
		Hudson	91,929	268,593
		James	22,726	93,964
		Potomac	1,409	2,446
		Susquehanna	39,634	34,361
		Subtotal	3,096,364	1,949,065
	E	Coastal	168,292	100,104
		Altamaha	6,462	6,896
		Neuse	16,517	13,133
		Roanoke	4,792	6,057
		Santee	45,462	33,573
		Savannah	6,499	7,954
		Subtotal	248,024	167,717
	F	Coastal	76,118	53,108
		Alabama-Tombigbee	22,762	24,890
		Apalachicola	57,096	27,223
		Subtotal	155,976	105,222
	G	Coastal	143,951	94,398
		Gulf coast refineries[b]	2,882	2,882
		razos	14,040	18,039
		Colorado (TX)	16,683	18,670
		Mississippi	525,638	525,638
		Rio Grande	20,042	54,982
		Sabine	5,330	8,734
		Trinity	66,565	29,572
		Subtotal	795,130	752,913
	H[a]	Coastal and inland rivers	157,387	108,189
	I	No urban areas	0	0
	J[a]	Coastal and inland rivers	83,810	57,612
	K	Coastal	260,566	123,976
	L	Coastal	109,253	54,349
		Sacramento	30,596	38,171
		San Joaquin	33,863	57,647
		Subtotal	173,711	150,168
	M	Coastal	84,521	67,725
		Columbia	17,959	38,206
		Subtotal	102,480	105,931
	N	Coastal	30,361	4,332
	O	Coastal	12,364	1,949
	P	Coastal	3,568	5,514
		Copper	0	0
		Susitna	0	0
		Subtotal	3,568	5,514
	Q	Coastal	0	0
		Yukon	0	0
		Subtotal[a]	5,009,464	3,443,557
Africa			356,249	244,889
Europe			4,506,162	3,097,582
Central America			328,984	226,147
South America			683,454	469,813
Asia			2,463,506	1,693,439
Oceania			289,851	199,247
TOTAL			13,637,670	9,374,694

NOTES: [a]Subtotal for North America does not include Coastal Zones in Mexico; [b]See Table F-4 for calculation of refinery loading.

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TABLE I-17 Comparison of STORET Oil and Grease Data Used in this Study with 1990s USGS Oil and Grease Data for Louisiana

Description	Delaware River	Mississippi River	USGS Data	All Data
Statistics				
Number of observations	99	46	704	849
Minimum concentration (mg L^{-1})	1.0	0.5	0.5	0.5
Maximum concentration (mg L^{-1})	122.7	6	81	122.7
Average concentration (mg L^{-1})	5.80	0.84	1.27	1.77
Standard deviation (mg L^{-1})	13.21	0.94	4.65	6.35
Percent exceedence				
Mississippi 1990s average = 0.84 mg L^{-1}	100 percent	24.6 percent	21.1 percent	30.4 percent
Delaware 1990s average = 5.80 mg L^{-1}	21.2 percent	2.3 percent	2.6 percent	4.7 percent

automobile exhaust based), and (2) fuel oil was completely consumed (i.e., there was no oily waste discharged by users of fuel oil), then the land-based sources would be derived only from the use of middle distillate fractions that end up on the land surface or in municipal and industrial discharges. Expressing the best estimate of the land-based oil that was returned to the sea as a fraction of the total middle distillate consumption gives a ratio of 3.4/320, or 1.1 percent, which is still a very small percentage.

Table I-18 shows comparisons of the computed land-based loads presented in the current study for North America and other locations with the BP Amoco (2000) data. Note the ratio of land-based sources was very consistent for all countries shown.

The best estimate of petroleum hydrocarbon loading from land-based sources was about 8 times smaller than the best estimate from the National Research Council (1985), and was much smaller than other previous world estimates (Table I-19). Although estimates presented here were considerably different than the studies in Table I-19, the calculations used in this analysis were based on more measured data than in these previous studies, including the National Research Council (1985). The approach used in the current study was also consistent with methods for estimating pollutant loads from urban runoff. The upper range of the current estimates agreed fairly well with previous studies, but the 1990s STORET data suggest that the best estimate may be much lower than previous studies indicated.

Literature-reported data and data provided by Baker (2001) on the Susquehanna River confirmed that the Michel (2001) data were within a reasonable range for river total PAH concentrations (Table I-20). In addition, estimation of river PAH concentrations were made using average annual flows calculated from available flow data (Table I-3) with PAH loadings calculated for corresponding rivers in this study (Table I-13). The average of these calculated concentrations ranged from 242 to 2,900 ng L^{-1}, with a best average concentration of 800 ng L^{-1} (Table I-21). While this concentration was greater than ambient river concentrations reported by other studies, it represents a conservative estimate of PAH concentrations in river water using the best available data. Furthermore, the calculated concentrations of PAH in the Mississippi River corresponded nicely with the range of total PAH measured by Michel (2001).

TABLE I-18 Comparison of Oil Consumption with Estimated Oil and Grease Loading from Land-based Sources to the Sea

Location	1999 Oil Consumption[a] (million tonne yr^{-1})	Oil and Grease Loading to the Sea from Land-based Sources[b] (million tonne yr^{-1})	Ratio of Oil and Grease Loading to the Sea to Oil Consumption (percent)
North America	1047.1	3.4	0.3
South and Central America	218.8	0.7	0.3
Europe	755.2	3.1	0.4
Africa	115.5	0.2	0.2

NOTES: [a]Source: BP Amoco (2000); [b]Calculated in this study.

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TABLE I-19 Comparison of Petroleum Hydrocarbon Loading Estimates from Land-based Sources from this Work and Other Studies

Reference	Comments	Hydrocarbon Loading (tonne yr^{-1})		
		Low	Best Estimate	High
World estimates				
Baker (1983)	Petroleum hydrocarbons from municipal wastes, industrial waste, and runoff	700,000	1,400,000	2,800,000
National Research Council (1985)	World estimate of land-based sources	600,000	1,200,000	3,100,000
Van Vleet and Quinn (1978)	Petroleum hydrocarbons *from municipal wastes only* based on Rhode Island treatment plants	—	200,000	—
This work	World estimate of land-based sources	6,800	141,000	5,000,000
Ratio (this work: National Research Council [1985]		0.01	0.12	1.61
North American estimates				
Eganhouse and Kaplan (1982)	US input of petroleum hydrocarbons based on mass emission rate for wastewater effluent in southern California	—	120,600	—
This work	North American estimate of land-based sources	2,500	52,000	1,800,000

TABLE I-20 Comparisons of Total PAH Concentrations in Literature, Baker (2001), and Michel (2001)

Reference	Description	Range or Average Measured Total PAH Concentrations (ng L^{-1})
Baker (2001)	Susquehanna River, Pennsylvania	17.01–150.81
Bidleman et al. (1990)	Sampit River, South Carolina	6.8
Gustafson and Dickhut (1997a)	Elizabeth River, Virginia	91.4
Gustafson and Dickhut (1997b)	York River, Virginia	29.15
Michel (2001)[a]	Mississippi River, Louisiana	100–156
Ollivon et al. (1999)	Seine River, France	94.44
Ollivon et al. (1999)	Marne River, France	148.35

[a]Data used in the current study.

TABLE I-21 Estimated Concentrations of Polycyclic Aromatic Hydrocarbon Concentrations Based on Calculated Loadings

River	Annual Flow (10^6 m^3 yr^{-1})	Estimated Concentration (ng L^{-1})		
		Low	Best	High
Columbia	220,892	19	26	320
Delaware	10,712	696	870	1,102
Hudson	12,365	242	3,258	4,127
James	6,209	168	2,270	2,875
Mississippi[a]	625,760	101	126	160
Neuse	3,524	404	559	6,902
Sabine	7,043	135	186	2,297
Sacramento	21,000	197	273	3,366
Susquehanna	36,779	101	140	1,730
Trinity	8,944	359	496	6,124
Average	95,323	242	820	2,900

[a]Estimated oil and grease loading for Mississippi River was the same for low, best and high estimates of PAH loading (see Tables I-12 and I-13).

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J

Methods Used To Estimate PAH Loadings to the Marine Environment

To understand the toxic effects of petroleum hydrocarbon releases to the coastal ocean, one has to examine the loading of the more toxic components of the hydrocarbon mixture. Since PAH are thought to be responsible for many of the biological effects of petroleum, the committee estimated PAH loads from various petroleum sources. This refinement of the 1985 National Research Council (NRC) report is a step toward a more rigorous risk assessment of petroleum releases to the coastal oceans. For many of the source types, including natural seeps, platforms (offshore andcoastal), pipelines (offshore and coastal), produced waters, vessel spills, vessel operations, aircraft dumping, two-stroke engines, vessels of less than 100 GT, and coastal facilities, PAH loadings were estimated as a fraction of the total petroleum hydrocarbon loadings, based on measured PAH content of crude oils and refined petroleum products. Environment Canada has measured the amount of a standard suite of PAH listed in Table J-1 in a variety of oils. These data were used to estimate the average total PAH amounts in five types of oils: crude oil, heavy distillates, light distillates, jet fuel, and lube oil (Table J-2). Additionally, the PAH content of gasoline was assumed to be negligible. The best estimates of petroleum hydrocarbon inputs to the sea by the sources discussed above were broken down into the six oil types (crude oil, heavy distillates, light distillates, jet fuel, lube oil, and gasoline), which were then multiplied by the appropriate fractions of PAH in the six types of oil to estimate the PAH contributions to the sea by source.

PAH loadings to North American coastal waters from the atmosphere were calculated for 21 individual PAH based on estimated PAH levels in the coastal atmosphere (Table 2-; see Chapter 3 and Appendix B for details). Because coastal waters are undersaturated with dissolved PAH relative to the overlying atmosphere, there is a significant net transfer of atmospheric PAH to the oceans. PAH loadings from land-based sources were estimated by assuming that the PAH load from each river is proportional to the estimated petroleum hydrocarbon loading (see Chapter 3 and Appendix I for details).

TABLE J-1 PAH Compounds Measured by Environment Canada

Naphthalene
C0-N
C1-N
C2-N
C3-N
C4-N
Phenanthrene
C0-P
C1-P
C2-P
C3-P
C4-P
Dibenzothiophene
C0-D
C1-D
C2-D
C3-D
Fluorene
C0-F
C1-F
C2-F
C3-F
Chrysene
C0-C
C1-C
C2-C
C3-C
Other PAH
Biphenyl
Acenaphthalene
Acenaphthene
Fluoranthene
Pyrene
Benz[*a*]anthracene
Benzo[*b*]fluoranthene
Benzo[*k*]fluoranthene
Benzo[*e*]pyrene
Benzo[*a*]pyrene
Perylene
Indeno[1,2,3*cd*]pyrene
Dibenz[a,h]nthracene
Benzo[*hi*]erylene

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TABLE J-2 Oils or Refined Products Used to Calculate Amount of PAH in Different Petroleum Hydrocarbons Discussed in This Report

Oil type	References (see codes)	Estimated PAH in oil
Crude (average of heavy and light crudes)		**0.013908**
Heavy crudes		
Alberta Sweet Mix Blend (ASMB)	*a, b*	
Arabian Light	*c, d, e*	
Arabian Light (Mackay)	*c, d, e*	
Brent oil (British)	*b*	
Granite Point, Cook Inlet	*b, f, g*	
Trading Bay, Cook Inlet	*b, f, g*	
Swanson River, Cook Inlet	*b, f, g*	
Federated	*h, i*	
Gul1faks oil (Norwegian)	*b*	
Norman Wells	*j, k, l*	
Nipisi oil	*m*	
Northern Pipeline	*b*	
Middle Pipeline	*b*	
Southern Pipeline	*b*	
Sahara Crude from Norway	*b*	
Statfjord (Norwegian)	*b*	
Prudhoe Bay from biodegradation	*j, k, l*	
Osenberg	*j, k, l*	
Bent Horn	*j, k, l*	
Light crudes		
Arabian Medium Crude	*b*	
Hedrun Crude	*b*	
Hibernia	*j, k, l*	
Lloydminster oil	*j, k, l*	
Terra Nova	*j, k, l*	
Russia Komi after water correction	*b*	
Heavy distillates (average of Bunker C and fuel oil marine diesel)		**0.024256**
Bunker C		
ESD Bunker C	*b, s*	
Bunker C from biodegradation	*j, k, l*	
1998 Quebec spill Bunker C type	*t*	
Irving Whale oil	*u*	
Fuel oil marine diesel		
Bunker C and diesel mixture	*b, f, g*	
Motor Vessel (MV) Attona	*b*	
MV Western	*b*	
MV-Paean vessel reduced	*b*	
MV-Paean vessel	*b*	
Intermediate Fuel Oil-30 viscosity	*b*	
Valery Chkalov	*b*	
Light distillates		**0.034441**
Diesel No. 2	*b, f, g*	
Diesel spill from Quebec 1998	*o, p*	
Mobile burn 97 diesel	*q*	
Mobile burn 98 diesel	*r*	
Jet fuel		**0.028373**
Jet B fuel	*f, g*	
Lube oil		**0.000118**
Lube oil	*j, k, l, n*	

Reference codes: [a]Wang et al. (1994); [b]Wang et al. (1999a); [c]Wang (1998b); [d]Wang et al. (2000c); [e]Wang et al. (in press); [f]Wang et al. (1997a); [g]Blenkinsopp et al. (1997); [h]Wang (1999); [i]Wang et al. (2001); [j]Wang (1994b); [k]Wang (1994c); [l]Wang et al. (1998a); [m]Wang et al. (1998b); [n]Wang (1994a); [o]Wang (1998a); [p]Wang et al. (2000b); [q]Wang et al. (2000a); [r]Wang (2000); [s]Wang et al. (1997b); [t]Wang et al. (1999b); [u]Wang (1995)

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K

Regulatory Framework

Just over one year after the *Exxon Valdez* ran aground on Bligh Reef, Congress passed, and President Bush signed, the Oil Pollution Act of 1990 (OPA). The Act was meant to be the primary federal legislation addressing oil spills into United States navigable waters and onto its shorelines. At the time of OPA's passage, the major issues confronting the Congress included the interplay of federal and state law on the subject, United States participation in international efforts to deal with oil spills, the continuing viability of the Shipowner's Limitation of Liability Act of 1851 (Limitation Act), and the nature and extent of recoverable damages, particularly for injured natural resources and purely economic losses.

There are numerous federal statutes dealing with oil discharge, but until the passage of the Oil Pollution Act of 1990 (the Act) none specifically addressed oil pollution to the nation's waterways and coastlines. A partial listing of current laws under which oil spill cleanups are regulated include: The Clean Water Act, Deepwater Port Act, Outer Continental Shelf Lands Act, Trans-Alaska Pipeline Authorization Act, and the Limitation of Liability Act. While the need for a unified oil pollution code was debated in Congress for more than a decade, it was the *Exxon Valdez* grounding that provided the impetus to pass the Oil Pollution Act, which was then signed into law on August 18, 1990.

There are many provisions of the OPA that, when taken as a whole, set this law apart from other oil pollution legislation. These are:

1. **OPA's purpose and intent was to provide a rapid legislative tool which would ensure a rapid and effective cleanup of oil spills to the nation's waterways and coasts.**

   Because of the many laws under which oil spill liability is regulated, the OPA was designed to be the legal framework of choice to direct the removal of oil spills on navigable waterways and to compensate affected parties. Toward this end, the OPA defines navigable waterways far more narrowly than the case law has defined such a waterway under the Clean Water Act. While the Clean Water Act can define a navigable waterway as wetlands, tributaries, and even groundwater, the OPA limits that definition directly to a discharge into a waterway that empties into a coastal region. Claimants seeking relief under the OPA for a discharge in an inland area, away from the coast and not within the exclusive economic zone (EEZ), have not been successful. Additionally, it should also be said that the OPA amends the Clean Water Act to allow the U.S. government to participate in removal, mitigation, and monitoring of discharge events.

   Only secondary to this primary purpose was to reduce the amount of litigation by the presence of a presentation requirement (33 U.S.C. § 2713)(OPA section 1013). Prior to the commencement of any legal action, those making OPA claims must first present them to the responsible party. The courts have upheld this requirement and have denied OPA relief if it has not been fulfilled. However, this presentation requirement should not be taken to mean that removal should not begin until this requirement has been met. Indeed, the courts have ruled that cleanup efforts may commence before a court has ruled on the presentation requirement.

2. **Responsible Parties**

   Section 1002 (Elements of Liability) defines responsible parties as, "a vessel or a facility from which oil is discharged, or which poses the substantial threat of a discharge of oil, into or upon the navigable waters or adjoining shorelines of the exclusive economic zone…"

   It is these responsible parties who must pay the costs associated with removal and monitoring efforts (monitoring efforts are included due to the language of section 1002(a), i.e., "…which poses the substantial threat

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of a discharge…", and section 1001(31), i.e., …, the costs to prevent, minimize, or mitigate oil pollution…). Responsible parties may be exempt from the limits to liability, as defined in 33 U.S.C. § 2704(c), for such things as gross negligence, violation of Federal safety, failure of the responsible party to report the incident, or failure to provide reasonable cooperation with the removal activities.

3. **The Act established the Oil Spill Liability Trust Fund (33 U.S.C. § 2712)**

   Affected parties may seek relief from this fund if full compensation is not first available from the responsible party.

4. **Non-preemption (Savings clause)**

   The OPA makes clear that the Act will not preempt any state from imposing any additional liability or requirements with respect to the discharge of oil or the removal activities (33 U.S.C. § 2717)(OPA section 1018(a)). As such, OPA claims may be brought in state or federal court.

   While many numerous damage claims can be compensated under the OPA, punitive damages are not. However, due to the non-preemption of the OPA, these claims may be sought under applicable state laws.

   There have been several court cases which address the OPA's savings clause. In Ray v. Atlantic Richfield Co (435 U.S. 151, 1978 AMC 527 (1978)) the U.S. Supreme Court held that the OPA's savings provisions only applied to those state laws which involve Title I issues (liability rules and financial requirements) to recover damages from vessels "from which oil is discharged, or which pose the substantial threat of a discharge of oil" (120 S. Ct. 1146). Therefore, states were free to set forth additional requirements that related to the discharge of oil or the threat of discharge. However, state laws will be preempted in areas that do not relate specifically to the state's or local concerns and responsibilities. For example, while a state may impose additional or stricter regulations to protect their waterways from oil discharges, a state is not within its jurisdiction to regulate tanker design or vessel personnel qualification. These matters will be regulated by federal statutes that seek to maintain uniformity throughout the states.

5. **Economic losses are recoverable under the OPA**

   Due to the limitations of admiralty tort law, which provides no compensation to parties who suffer economic losses in the absence of physical harm, the OPA specifically address this deficiency through section 1002 of the OPA. This section states that "…economic losses resulting from destruction of, real or personal property… shall be recoverable…" (OPA section 1002(B)). OPA also allows for recovery of lost profits or loss of earning capacity as a result of the damage to real or personal property (OPA section 1002(E)). However, the Act does not make clear when these damages are recoverable.

   The case law on this subject has been somewhat inconsistent. In a Petition of Cleveland Tankers, Inc (791 F. Supp. 669, 1992 AMC 1727 (E.D. Mich. 1992)) the courts dismissed because Cleveland Tankers did not allege any injury, destruction, or loss to their real or personal property. Most other courts have interpreted section 1002 more broadly and have regularly awarded damages to parties who have suffered some economic loss due to a spill (Sekco Energy, Inc. v. M/V Margaret Chousest (820 F. Supp. 1008, 1994 AMC 1515 (E.D. La. 1993), Ballard Shipping Co. v. Beach Shellfish (32 F.3d 623, 1994 AMC 2705 (1st Cir. 1994)). This seems to be more in line with the intent of the OPA.

6. **OPA preempts the Limitation of Liability Act.**

   For vessels, the Limitation of Liability Act limits the recoverable damages to the vessel's value plus freight owing at the end of a voyage. The case law has demonstrated that the purpose of the OPA was to encourage rapid cleanup by responsible parties, and that any limitation of liability is at cross purposes to this goal. Therefore, the OPA preempts the Limitation of Liability Act under federal or state law.

7. **Natural resources losses may be assessed by active-use and passive-use.**

   This is possibly the most debated of the OPA's provisions due to the lack of specific guidelines directing the assessment of natural resource losses. Active-use resources are those that are used; passive-use describe those resources which may not be used, or even plan to be used by anyone, but are nevertheless valued as available.

   Trustees may use any manner of valuation techniques to assess natural resource loss including contingent evaluation. This process requires that a valuation measure be determined by surveying members of a hypothetical market and asking them how much they would pay to preserve that resource. While this technique seems subjective, the courts have given trustees great deference as long as the study is performed properly. It is likely that in the future such vague valuation processes will give rise to further litigation.

8. **Definition of reasonable recovery costs**

   While the Act does define cleanup costs under sections 1012(a) and 1001(31), it was left to the courts to further define and uphold the clear language of those sections. Much of the controversy surrounding this section has centered on the inclusion of mitigation and monitoring costs associated with a spill, and whether those costs may be recovered from the Oil Spill Liability Trust Fund. In general, the courts have pointed to the language of section 1001(31) which states that removal costs means "the costs of removal that are in-

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curred after a discharge of oil has occurred or, in any case in which there is a substantial threat of a discharge of oil, the costs to prevent, minimize, or mitigate oil pollution from such an incident." Monitoring is thus necessary to prevent, minimize, or mitigate a discharge. Additionally, while the Trust Fund is available for monitoring and mitigation costs, the responsible party is also liable for these as well.

The case law has also further defined recovery costs associated with a discharge to include incremental costs. That is, salaries may also be figured into recovery costs for the time during which government employees (e.g., Coast Guard, attorney's fees) spend monitoring a spill (United States v. Hyundai Merchant Marine Co (172 F.3d 1187, 1999 AMC 1521 (9th Cir.), cert. Denied, 528 U.S. 963 (1999)).

Finally it is worth noting that nowhere in OPA does it define what "all removal costs incurred by the United States" means specifically. Therefore, the Ninth Circuit's reading of the liability provisions, as applied to United States v. Hyundai, defines removal costs to include all costs that are "prudent, necessary, or reasonable," and is limited to the extent that the government does not act arbitrarily or capriciously.

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