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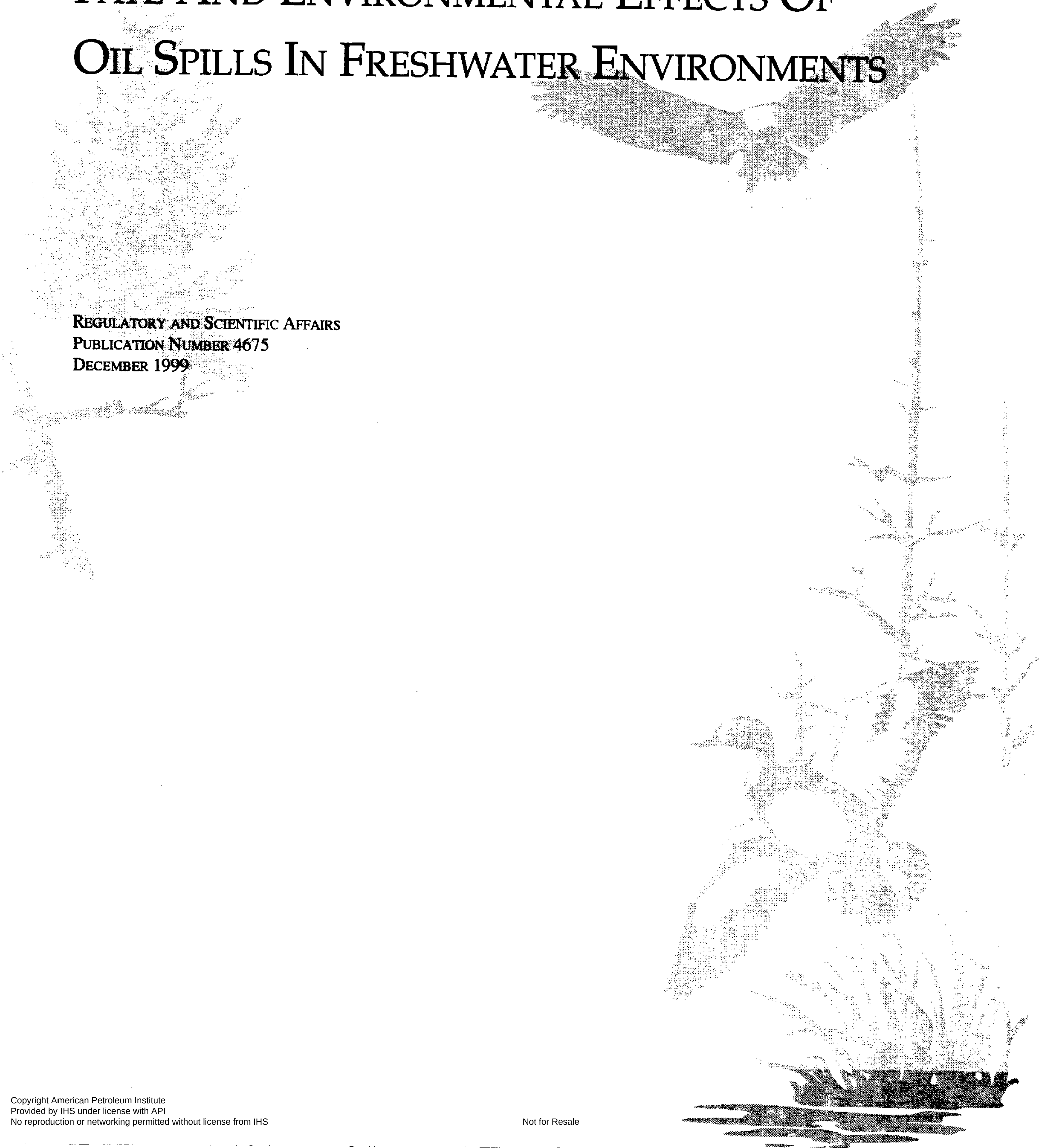
FATE AND ENVIRONMENTAL EFFECTS OF OIL SPILLS IN FRESHWATER ENVIRONMENTS



REGULATORY AND SCIENTIFIC AFFAIRS
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Fate and Environmental Effects of Oil Spills in Freshwater Environments

Regulatory and Scientific Affairs

API PUBLICATION NUMBER 4675

EDITED BY:

DAVID STALFORT, U.S. COAST GUARD

DECEMBER 1999

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API STAFF CONTACT

Alexis Steen, Regulatory and Scientific Affairs

MEMBERS OF THE OIL SPILLS SCIENCE AND TECHNOLOGY WORK GROUP

David Fritz, Chairperson, BP Amoco
Dan Allen, Chevron North America E&P Company
Ken Bitting, US Coast Guard R&D Center
Bon Britton, US Fish and Wildlife Service
Michael Carter, US Maritime Administration
Jim Clow, Equiva Services
Bill Dahl, Exxon Research & Engineering Co.
Donald Erickson, Bay West, Inc.
Ronald Goodman, Imperial Oil Ltd.
Brad Hahn, State of Alaska
Bela James, Equilon Enterprises, LLC
Robin Jamail, Texas General Land Office
Roger LaFerriere, US Coast Guard
Jerry Langley, Williams Pipe Line Company
Stephen Lehamann, NOAA
Richard Lessard, Exxon Research and Engineering Company
Dan Leubecker, US Maritime Administration
Edwin Levine, NOAA
Jason Maddox, NOAA
Joseph Mullin, Minerals Management Service
Douglas O'Donovan, Marine Spill Response Corporation
W. Michael Pittman, US Coast Guard
Ninette Sadusky, US Navy SUPSALV
Jim Sanders, CITGO Pipeline Company
Dana Slade, Lakehead Pipe Line Company
Jean Snider, NOAA
Robert Urban, PCCI
Carol Voigt, CITGO Petroleum Corporation

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

EXECUTIVE SUMMARY

This report summarizes and documents potential environmental effects from inland oil spills into fresh surface waters. It identifies, describes, and compares the behavior, fate, and ecological implications of crude oil and petroleum products in inland waters. The document is intended to provide basic information necessary for the formulation of spill response strategies that are tailored to the specific chemical, physical, and ecological constraints of a given spill situation. It is not a spill response manual with step-by-step instructions for the selection and implementation of response methods, nor does it address oil spill prevention. In separate chapters, the report:

- describes the relevant features of various inland spill habitat types;
- discusses the chemical characteristics of oils and the fate processes that are dependent thereon; and
- summarizes reported results of ecological and toxicological effects both generally and with specific references to distinct organism groupings.

This research effort was sponsored by the American Petroleum Institute (API) to provide technical information for persons responsible for inland spill response and cleanup, for researchers, and for others dealing with protection of the environment from possible oil spill hazards. API recognized a need to compile information on oil solubility, biodegradation, transport phenomena, sediment interactions, bioavailable fractions, bioconcentration potential, toxicity, and organism behavioral effects to facilitate the selection of spill responses that minimize environmental damage and optimize effectiveness.

Information sources included case histories, field research projects, and laboratory experiments. The authors performed a systematic survey of published literature using keyword searches of several commercially available abstract databases. Additional literature was obtained directly from numerous researchers in the field. Prior reviews and syntheses of oil spill fate and effects information are identified throughout the document. Information specific to the marine environment was borrowed only where applicable or where freshwater information was not available.

Significant findings of this review include the following:

- Inland water habitats susceptible to oil spill effects were categorized as follows: open water, large rivers, small lakes and ponds, small rivers and streams, bedrock, manmade structures, sand, mixed sand and gravel, gravel, vegetated shorelines, mud, and wetlands. The respective sensitivities of these habitats to oil spill impact depend on substrate permeability, the extent of physical removal rates by currents, and the extent of use by animal and plant communities. Mud and wetland habitats tend to be most sensitive to oiling, and open waters, large rivers, and sand habitats least sensitive. Unfortunately, the ease of oil removal tends to be inversely proportional to habitat sensitivity.

- Processes affecting the fate and behavior of spilled oil in inland waters include spreading and drift, emulsification and dispersion, evaporation, dissolution, sorption/sedimentation/sinking, photodegradation, and biodegradation. The rate at which each of these occurs will be regulated both by prevailing environmental conditions and by the chemical makeup of the spilled product. In general, lighter molecular weight constituents and lighter, more refined, products will be more susceptible to the fate processes listed. Although the lighter oils remain in the environment for a shorter time, they tend to be more toxic to aquatic species than the heavier oils.

- Spilled oil products will affect freshwater organisms both directly, as a result of physical and toxicological processes, and indirectly, as a result of habitat impacts, nutrient cycling disruptions, and alterations in community and trophic relationships. An oil's toxicity is primarily a function of the solubility of its components in water. Toxicity should be predictable from an oil's composition and that of its water soluble fraction (WSF), especially its aromatic content. It is a generally accepted conclusion that the higher an oil's concentrations of polyalkylated mono- and diaromatic constituents, the more toxic the oil. Thus refined petroleum products and lighter oils tend to be more toxic than heavier crudes and weathered products.

- Immediately following an oil spill, effects on aquatic plants and animals tend to be due to the physical coating or entrapment of exposed organisms. Membrane damage, respiratory blockage, loss of insulation and buoyancy, smothering of sediments, and disrupted swimming and feeding behaviors each may contribute to the initial loss of organisms from within a spill zone. Additional toxic effects may occur as a result of the dissolution of oil constituents in water, and numerous laboratory studies describe the toxic responses of organisms to oil exposure. However, post-spill field observations suggest that the toxicological effects of spilled oil tend to be less extensive than the physical ones. The extent of direct physical exposure of organisms to spilled, undissolved product seems to be the primary determinant of organism effects. The greater the probability that a plant or animal will directly encounter spilled product before the oil has had a chance to weather or dissipate, the greater the chance that organism will be adversely affected by the spill.

- Secondary effects of oil spills can also have dramatic impacts on ecological communities, including alterations in nutrient cycling, reductions in dissolved oxygen concentrations, decreases in species diversity, loss of habitat, and disruptions of trophic relationships. Each effect may produce adverse consequences to ecosystems exposed to spilled oil.

Based on this review, five areas for future research on freshwater spills were identified. They are:

- Testing of WSF toxicity and method standardization;
- Weathered oil and ultraviolet(UV)-enhanced polyaromatic hydrocarbon (PAH) toxicity;
- Long term fate and effects of oil in sediments;
- Sensitivity of plants to oiling and their resiliency to cutting; and
- Toxicological and physical effects from oil exposure to amphibians, reptiles, and mammals.

Greater documentation is needed regarding inland oil spill ecological investigations and response case histories to facilitate efficient and effective response efforts in the future.

Ecological pragmatism and response experience may be nearly as important as technical expertise in formulating and implementing a successful spill response. In reality, economic and political considerations will often predominate over ecological ones in formulating spill response strategies. The combination of these considerations will usually mean that some type of response is mandated in nearly every spill situation. By being aware of basic technical information regarding the fate and effects of spilled oil in inland waters, spill responders should better be able to determine appropriate response strategy under any scenario.

Section 1
INTRODUCTION

BACKGROUND OF THE REVIEW

Numerous studies have investigated the fate of oil spilled into aquatic systems and have documented potential adverse effects. However, these studies have focused primarily on marine systems. This report reviews the fate and effects of spilled petroleum products into inland or freshwater environments. It focuses on ecological effects and toxicity to aquatic and wildlife species only. The report seeks to combine the knowledge gained from laboratory research and field observations to enhance the overall understanding of spilled oil's behavior in the freshwater environment.

The American Petroleum Institute (API) has focused several projects on issues related to freshwater oil spills, including: reviews of natural resource damage assessments (API, 1992a,b), a review of the impact on the environment of cleanup practices (Vandermeulen and Ross, 1991), a workshop and a subsequent manual on the environmental effects of response technologies for inland waters (API, 1995a), and an annotated bibliography in electronic file format of oil spills into inland waters from 1946-1993 (API, 1997). The effects of oil spilled in freshwater have been considered in previous reviews including: Vandermeulen and Hrudey (1987), Green and Trett (1989), API (1992a), and API (1992b,c). These documents comprise topic-specific articles on oil in the environment (Vandermeulen and Hrudey, 1987), bibliographic lists (API, 1992a), comprehensive discussions of the fate and behavior of oil and toxicity of both hydrocarbons and oil (Green and Trett, 1989), and reviews of assessed damages from oil spills into inland waters (API, 1992b,c).

Because most catastrophic spills due to transportation of crude oil and refined products have been largely over open seas or along ocean coasts, the perception of environmental risk has traditionally focused on marine and brackish aquatic habitats. Comparatively less attention has been directed toward the potential problems of contamination of inland waterways. However, many ports are located in or near freshwater. Furthermore, the transportation of petroleum products is not confined to seagoing vessels, but is often accomplished by inland barges, pipelines, railways, and highways. Accidents involving inland transport can result in significant releases of crude oil or petroleum products into freshwater systems. The Ashland oil spill into the Monongahela River in 1988 demonstrated that freshwater oil spills can be as dramatic and as difficult to control as marine or coastal spills. Nearly 4 million gallons of No. 2 diesel fuel were released from a collapsing storage tank. An estimated 750,000 gallons entered the Monongahela River, moved past Pittsburgh, and into the Ohio River, forcing several drinking water plants to close their intakes.

Although the processes affecting the fate of petroleum products do not differ substantially between marine and freshwater systems, the behavioral dynamics can be quite distinct. The sheer volume of the marine system and the influence of tides and currents mean that spilled oil will distribute and persist much differently in the world's oceans than in its freshwater lakes, rivers, wetlands, creeks, and ponds. Evaporation, biodegradation, photooxidation, emulsification, and dissolution occur in fresh and marine systems according to the same chemical and physical processes. However, the rates at, and the degrees to, which they occur can vary dramatically. For that matter, they can deviate significantly among different types of freshwater habitats. Oil will persist, disperse, and degrade at different rates in rivers and lakes. Biodegradation will proceed much faster in an eutrophic (nutrient rich) temperate wetland than an oligotrophic (nutrient-poor) arctic pond or river.

Likewise, the types of ecological effects to be expected following an inland spill, as opposed to a marine spill, can be substantially different. While threats to migrating fish stocks or aquatic mammals may be primary concerns following an ocean spill, adverse effects to benthic insects, reptiles, waterfowl, or shoreline vegetation may be the focus of a freshwater event. Also, the extreme diversity among freshwater habitats means that effects resulting from the spill of a given quantity of a given petroleum product can vary immensely between different inland spill events.

The chemistry of a petroleum product will generally be the principle determinant of its fate and effect once spilled into the environment. Laboratory research suggests that behavior and toxicity can be best understood in terms of the properties and relative concentrations of the constituent hydrocarbons present in the product spilled. But knowledge of the chemical composition of a product will go only so far towards facilitating predictions of how oil will behave and affect exposed organisms under real world conditions. Factors which are not considered in laboratory studies but which may be primary determinants of the fate and effects of spilled oil in freshwater environments include the presence/absence of current, shoreline complexity, nutrient concentrations, water temperature, historical exposure to petroleum products, and time of year. Realistically, the manner and extent of the influence that these factors have on the fate and effects of spilled petroleum can be discerned only by reviewing post-spill field studies reported in the literature.

OBJECTIVES AND ORGANIZATION OF THE REVIEW

The objectives of this report were to review:

(1) the environmental characteristics of different freshwater habitats that influence the behavior and effects of spilled oil;

(2) the chemical characteristics of petroleum products that may be strong determinants of the behavior and effects of spilled oil;

(3) the specific chemical, physical, and biological processes controlling the fate of oil in the freshwater environment;

(4) the ecological effects of petroleum products on specific freshwater organism types; and

(5) to identify research needs.

The review specifically addresses releases of petroleum products and crude oils into surface freshwater habitats. Literature and documentation of oil spills into inland waters from various sources were accessed. The information included case histories, field research projects, and laboratory experiments. A systematic survey of published literature was done using keyword searches of several commercially available abstract databases. Additional literature was obtained directly from numerous researchers in the field.

The report provides information about freshwater habitats, plus information about the characteristics and behavior of oil, to enable response planners and decision makers to better predict the ecological effects of an oil spill.

Information about freshwater habitats + Information about the characteristics and behavior of oil = Greater ability to predict the ecological effects

The report is organized into the following sections:

Section 2 describes the characteristics of multiple freshwater habitat types. Specific habitat factors are discussed in terms of their influence on the behavior and effect of spilled oil and their bearing on the selection of appropriate spill response strategies.

Section 3 describes the chemical characteristics of petroleum products and their hydrocarbon constituents. It then applies this information in a discussion of the processes controlling the behavior of spilled oil and the factors that mitigate those processes.

Section 4 describes the ecological effects of spilled oil in freshwater environments. It reviews the toxicity of specific hydrocarbon constituents and whole oils. The relevance of testing and reporting methods and organism exposure conditions to the proper understanding of petroleum's effects on freshwater organisms is discussed. Reported effects of petroleum exposure on specific categories of freshwater organisms are reviewed.

Section 5 summarizes the findings from this review and then identifies where further research might contribute to an improved understanding of freshwater oil spills and selection of effective spill response actions.

Finally, Appendix A presents case histories that may provide responders with valuable information for minimizing the effects of oil spills in freshwater environments.

Section 2

DESCRIPTION OF FRESHWATER HABITATS

The following habitat descriptions, summarized in Table 2.1, are taken from *Options for Minimizing Environmental Impacts of Freshwater Spill Response* (API, 1995a). In general, for the purpose of this review, "sensitivity" will be judged on the basis of ecological factors. However, habitats can be considered sensitive because of human use (e.g., recreational beaches). This information is provided to improve the understanding of the fate of oil spilled into the various habitats.

Table 2-1. Freshwater environments and shoreline habitats correlated with the environmental sensitivity index (ESI) shoreline ranking for the Great Lakes.

Environment	ESI Ranking	Description
Water Environments		
Open Water		
Large Rivers		
Small Lakes and Ponds		
Small Rivers and Streams		
Shoreline Habitats		
Bedrock	ESI = 1A	Exposed rocky cliffs
	ESI = 2	Shelving bedrock shores
	ESI = 8A	Sheltered rocky shores
Manmade Structures	ESI = 1B	Exposed solid seawalls
	ESI = 6B	Riprap structures
	ESI = 8B	Sheltered solid manmade structures
Sand	ESI = 4	Sand beaches
Mixed Sand and Gravel	ESI = 3	Eroding scarps in unconsolidated sediment
	ESI = 5	Mixed sand and gravel beaches
Gravel	ESI = 6A	Gravel beaches
Vegetated Shorelines	ESI = 9A	Sheltered low vegetated banks/bluffs
Mud	ESI = 9B	Sheltered sand/mud flats
Wetlands	ESI = 10A	Fringing marshes
	ESI = 10B	Extensive marshes

Source: API, 1995a.

WATER ENVIRONMENTS

Open Water

Open-water environments exist in large water bodies, such as the Great Lakes, Lake Champlain, and Lake Mead. These large water bodies have ocean-like wave and current conditions; however, lake currents are generally weak (less than one knot). Local weather conditions commonly cause sudden changes in wave conditions. Suspended sediment loads are highly variable, both spatially and over time. River mouths are particularly problematic areas, with high suspended sediment and debris loads, shallow water zones, and manmade structures, which create complex water circulation patterns. The relative absence of tides results in a narrower oil zone on shorelines.

Thermal stratification with an upper, warm layer over cool, denser water is a common feature of large lakes during warmer months. In most temperate lakes, stratification ends in the autumn when surface cooling combines with water mixing from high winds. Ice formation is a common characteristic of interior and northern lakes in winter months. Although all inland waters are surrounded by land, response operations for open-water environments are water-based; that is, protection and recovery equipment must be deployed from vessels.

Open waters are considered to have low to medium sensitivity to oil spill impact because physical removal rates are high, water column concentrations of oil can be rapidly diluted, and most organisms are mobile enough to move out of the area affected by the spill. Enclosed and protected areas of large lakes are more sensitive than offshore and nearshore waters because of slower dilution rates. Oil spills can affect fish in the water column, with the early life stages at greatest risk. Also, many birds feed and rest on the water and, therefore, are highly vulnerable. Human use of affected areas may be restricted for a period of time, potentially limiting access for navigation, transportation, water intakes, or recreational activities during the spill response.

Free-floating flora or mats can occur in sheltered bays of nutrient-rich lakes. Mats may be particularly susceptible to oil because they are located in bays where oil may accumulate.

Moreover, the plants are at the water surface (where the oil is) and do not have underground roots that regenerate after being oiled.

Large Rivers

Large rivers have varying salinities, meandering channels, and high flow rates (currents usually greater than one knot). If they are navigable by large vessels, the environment can include associated locks, dams, pools, and other manmade structures. Examples of large rivers include the Mississippi River and its major tributaries, the Hudson River, the Delaware River, and the Columbia River. Water levels vary seasonally, with the potential for reversal of water flow up tributaries and into backwater lakes during high water. Floodplains are common characteristics of large rivers. Floods generate high suspended sediment and debris loads. There also can be small tidal effects. In northern regions, ice covers the surface in winter.

Large rivers have medium sensitivity to oil spill impact. Even though they have high natural removal rates, they have extensive biological and human use. Biological resources of concern include concentrations of migratory waterfowl and shorebirds, fish, and mussel beds. Under flood conditions, river floodplains contain highly sensitive areas that are important habitats for many valuable species. Floating vegetation is present in areas of low flow. Recreational use of rivers is very high, and many are major transportation corridors. Drinking, industrial, and cooling water intakes are quite vulnerable to oil spills in this environment because of turbulent mixing, and intakes often are shut down when slicks are present.

High currents, eddies, mid-river bars, ice formation, and flooding may complicate response measures in this habitat. Water flow across weirs and dams is of special concern because it is often turbulent and likely to emulsify oil slicks as they pass over these structures. The density of oil increases when emulsified. Emulsified oil can readily suspend beneath the surface and remain in the water column as it moves through a series of locks and dams. Additionally, oil can adsorb onto sediment particles, which then settle out in quiet backwaters, contaminating these habitats.

Small Lakes and Ponds

Lakes and ponds are standing bodies of water of variable size and water depth. Waves and currents are generally very low, although the water surface can become choppy. Water levels can fluctuate widely over time, particularly on manmade lakes. Smaller ponds can completely freeze over in winter. The bottom sediments close to shore can be soft and muddy, and the surrounding land can include wet meadows and marshes. Floating vegetation can be common.

The rate of water exchange is highly variable within this group, ranging from days to years. These water bodies can include sections of a river with low flow rates (e.g., behind diversion dams) or sections that are somewhat isolated from regular flow (e.g., backwater lakes or oxbow lakes). Isolated water bodies, such as kettle lakes, are unique members of this category because they have no surface water outflow and, therefore, have very low flushing rates. In shallow water, boat operations would be limited and most response operations would be conducted from shore.

Small lakes and ponds have medium to high sensitivity to oil spill impact because of low physical removal rates, limited dilution and flushing of oil mixed into the water column, and high biological and human use. They provide valuable habitat for migrating and nesting birds and mammals, and support important fisheries. Small lakes can be the focus of local recreational activities. Associated wetlands have higher sensitivities and are discussed at the end of this section.

Wind will control the distribution of slicks, holding the oil against a lee shore or spreading it along shore and into catchment areas. Wind shifts can completely change the location of slicks, contaminating previously clean areas. Thus, early protection of sensitive areas is important. The inlet and outlet are key areas on which to focus protection efforts. Oil impacts on floating vegetation depend to a large degree on dose, with possible elimination of plants at high doses.

Small Rivers and Streams

Small rivers and streams are characterized by shallow water (generally 1-2 meters) and narrow channels. Water flow can be highly variable, both throughout the seasons and with distance downstream. This group includes a wide range of waterbodies, from fast-flowing streams with low falls and numerous rapids over bedrock and gravel, to slow-moving bayous bordered by low muddy banks and fringed with vegetation. Sections of the channel may be choked with log jams and debris, and mid-channel bars and islands can divide water flow into multiple channels. Both boat and vehicular access can be very limited; often the only access will be at bridge crossings. Ice may further complicate response measures in this habitat.

Small rivers and streams have medium to high sensitivity to oil spill impact. Oil spills may have more of an impact on small rivers and streams than on large rivers due to a variety of conditions, such as lower flow conditions, lower dilution rates, lower overall energy, and a greater range of natural habitats. Fish spawn in streams and tributaries of larger rivers; thus, the most sensitive, early-life stages can be present. Fringing wetlands and adjacent floodplains are closely connected to small rivers and streams and are areas of high biological use and low natural removal rates.

Slicks usually contaminate both banks of small rivers and streams. Non-viscous oils are readily mixed into the entire water column in shallow streams, potentially exposing both aquatic and benthic organisms to oil. Initial weathering rates may be slower because spreading and evaporation are restricted in narrow channels and heavy vegetation cover. Fish kills are possible for spills ranging from gasoline to medium crude oils. Many different kinds of mammals, birds, reptiles, and amphibians use the stream bank habitats, and there can be localized high mortality rates of these animals. Spills can cause closure of water intakes for drinking water, irrigation, or industrial use along small rivers. A more aggressive response may be appropriate to prevent contamination of downstream habitat, particularly if water intakes, populated areas, or special habitat resources are present.

SHORELINE HABITATS

Bedrock

This shoreline type is characterized by an impermeable rocky substrate. The rock surface can be highly irregular, with numerous cracks and crevices. The slope of the shoreline varies from vertical rocky cliffs to shelving bedrock shores where flat or gently dipping rock layers have been cut by waves into wide platforms. Bedrock habitats are exposed to wide ranges in wave energy; headlands in the Great Lakes and other large lakes are the most exposed and bedrock shorelines in sheltered lakes are the least exposed. There can be a thin veneer of sand and gravel sediments on the rock platforms, although storm waves will strip these sediments from exposed shorelines. Boulder-sized debris can accumulate at the base of exposed rocky cliffs.

Bedrock shoreline habitats have a wide range of sensitivities to oil spills, depending upon their degree of exposure to natural removal processes. They have few attached organisms and plants, and rocky shore productivity is typically low. However, they may provide shelter to fish and nesting sites for birds that can be present in large numbers in nearshore waters.

In *exposed* settings, oil may be partially held offshore by wave reflection from steep cliffs and platforms. Any oil that is deposited will be rapidly removed from exposed faces, although oil persistence on any specific shoreline segment is related to the incoming wave energy during, and shortly after, a spill. The most resistant oil would occur as a patchy band at or above the high water line or would be deposited in any surface sediment.

In *sheltered* settings, oil will readily adhere to the rough rocky surface, forming a distinct band along the water line. Cracks and crevices will be sites of oil pooling and persistence. Oil will also penetrate and persist in any surface sediments. Medium to heavy oils can be very sticky and form thick black bands, while lighter oils are more readily removed by wave action, evaporation, and response efforts.

Manmade Structures

Manmade structures include vertical shore protection structures such as seawalls, piers, and bulkheads, as well as riprap revetments and groins, breakwaters, and jetties. Vertical structures can be constructed of concrete, wood, and corrugated metal. They usually extend below the water surface, although seawalls can have beaches or riprap in front of them. Riprap revetments are constructed of boulder-sized pieces of rock, rubble, or formed concrete pieces (e.g., tetrapods) placed parallel to the shoreline for shore protection. Riprap groins are oriented perpendicular to the shore to trap sediment; jetties are designed to protect and maintain channels; and breakwaters are offshore structures constructed to protect an area from wave attack. Riprap structures have very large void spaces and are permeable, whereas seawalls and bulkheads have impermeable, solid substrates. Manmade structures are very common along developed shores, particularly in harbors, marinas, and residential areas. The range in degree of a structure's exposure to waves and currents varies widely, from very low in dead-end canals, to very high on offshore breakwaters. Boat wakes can generate wave energy in otherwise sheltered areas.

Manmade structures have a range of sensitivities to oil spills, depending on the degree of exposure to natural removal processes. Biological communities may be sparse. Often, there are sources of pollutants or habitat degradation nearby, such as urban runoff, chronic small oil spills in marinas, poor water quality, and limited water circulation. More intrusive cleanup techniques are often conducted due to the lower biological use, higher public demand for oil removal for aesthetic reasons, and need to minimize human exposure to oil in populated areas. Manmade structures can vary in permeability, cohesion, and mobility and, in turn, how they are affected by oiling.

Vertical structures are generally impermeable to oil penetration, but oil can heavily coat rough surfaces, forming a band at the water line. During storms, oil can splash over the top of structures and contaminate terrestrial habitats. Riprap poses significant cleanup problems because of large void spaces between the riprap and heavy accumulations of debris. Large amounts of oil can become trapped in the riprap, where it is difficult to remove, and the oil can become a potential source of sheening.

Sand

Sand habitats have a substrate composed of sediments that are predominantly finer than 2 millimeters in diameter but greater than silt or clay-sized material (API, 1995a). The shoreline may consist of well-sorted sands of one principal size, or of poorly sorted mixtures of muddy sand, gravelly sand, or a combination of these two sands. When the sediments are fine-grained sand, beaches may be wide and flat; where the sediments are coarse-grained sand, beaches usually are steeper and narrower. Sandy shorelines may be naturally eroding, accreting, or stable, and groins or breakwaters may be placed to trap sand and maintain some beaches. Exposed sand beaches can undergo rapid erosion or depositional changes during storms. In developed areas, sand beaches can be artificially created by man and are commonly used for recreation. Sand bars and banks along rivers are included in this habitat.

Sand habitats have low to medium sensitivity to oil spills. They generally do not have sizable biological communities except where the habitat tends to be protected and consists of poorly sorted muddy sediments. Thus, ecological effects are likely to be limited because of the low natural biological productivity. In developed areas, sand beaches are considered sensitive because of their high recreational use.

During small spills, oil will concentrate in a band along the swash line. Maximum penetration into fine-grained sand will be less than 15 centimeters; penetration in coarse sand can reach 25 centimeters or greater. Clean sand can bury oiled layers quickly, making cleanup more complex. On heavily used recreational beaches, extensive cleanup is usually required to remove as much of the oil as possible. When large amounts of sediment must be removed, it may be necessary to replace these sediments with clean material. Traffic on sand can push oil deeper.

Mixed Sand and Gravel

Mixed sand and gravel habitats are characterized by a substrate that is composed predominantly of a mixture of sand- to cobble-sized sediments. These habitats may vary from a well-sorted cobble layer overlying finer-grained (sand-sized) sediments to mixtures of sand, pebble, and cobble. Typically, well-sorted beaches are exposed to some wave or current action that separates and transports finer-grained sediments; however, the sediment distribution does not necessarily indicate the energy at a particular shoreline. On depositional beaches, multiple berms can be formed at the different water levels generated during storms. In glaciated areas, the gravel component can include very large boulders. Natural replenishment rates are very slow for gravel in comparison to sand. Beaches along the Great Lakes and point bars along rivers and streams are mixed sand/gravel habitats.

Mixed sand and gravel habitats have medium sensitivity to oil spills. Biological communities are very sparse because of sediment mobility, potential for desiccation, and low organic content. Most invertebrates living in this habitat are deep burrowers, such as some oligochaete worms and insect larvae. Characteristic insects are mayflies, stoneflies, caddisflies, and midges, although mayflies and stoneflies are scarce or absent where silt is present. The nearshore habitat is used by fish for spawning and protects fry and larvae. Limited numbers of birds and mammals also are found in nearshore habitats.

Viscous oils reaching these mixed habitats may not penetrate into the sediments because the pore spaces between sediments are filled with sand. Therefore, deep oil penetration and long-term persistence are lower than on gravel substrates. However, oil can be found at depths below those of annual reworking, particularly if the oil is deposited high on the beach out of the reach of normal wave activity or is rapidly buried. Erosion can be a concern when large quantities of sediment are physically removed. In more sheltered areas, asphalt pavements can form if heavy surface oil deposits are not removed. Once formed, these pavements are very stable, can persist for years, and are chemically inert. Such pavement can be similar to bedrock habitats.

Gravel

Gravel habitats are characterized by a substrate that is composed predominantly of gravel-sized sediments. By definition, gravel includes sediments ranging in size from granules (greater than 2 millimeters) to boulders (greater than 256 millimeters). The sand fraction on the surface is usually less than 10%, although the sand content can increase to 20% with depth. These sediments are highly permeable because there are few sand-sized sediments to fill the pore spaces between the individual gravel particles. Gravel substrates may also have low bearing capacity and, consequently, may not support vehicular traffic. Typically, well-sorted beaches are exposed to some wave or current action that reworks the sediments and removes the finer-grained sediments. However, the sediment distribution does not necessarily indicate the physical energy at a particular shoreline; sheltered beaches can still have a large gravel source. In glaciated areas, the gravel can include very large boulders. On depositional beaches, zones of pure pebbles or cobbles can form multiple berms at the different water levels generated during storms. Gravel shorelines tend to be steeper than those composed of sand or mud. Natural replenishment rates are very slow for gravel as compared to sand. Examples of gravel habitats include beaches along the Great Lakes and bars along rivers and streams.

Gravel habitats have medium sensitivity to oil spills. Biological communities are very sparse because of sediment mobility, potential for desiccation, and low organic matter. Characteristic insects are mayflies, stoneflies, caddisflies, and midges, all with larvae living among the sediments. Flatworms, leeches, and crustaceans may be found on the gravel undersides. The nearshore habitat is used by fish for spawning and provides protection for fry and larvae.

Gravel habitats are ranked higher in sensitivity than sand and gravel habitats because deep penetration of stranded oil into the permeable substrate is likely. Oil can penetrate to depths below those of annual reworking, resulting in long-term persistence of the oil. The slow replenishment rate makes removal of oiled gravel highly undesirable. Formation of persistent asphalt pavements is likely where there is high accumulation of persistent oils.

Vegetated Shorelines

Vegetated shoreline habitats consist of the non-wetland vegetated banks that are common features of river systems and lakes. Bank slopes may be gentle or steep, and the vegetation consists of grasses, bushes, or trees common to the adjacent terrestrial habitats. The substrate is not water-saturated and can range from clay to gravel. The banks may flood seasonally and are exposed to relatively high-energy removal processes, at least periodically. Along undeveloped shorelines, there can be leafy litter and wood debris trapped among the vegetation. In developed areas, yards and gardens may abut the lake or river.

Vegetated shoreline habitats are considered to have medium to high sensitivity to oil spills. They are not particularly important habitats for sensitive animals and plants, although many animals use vegetated banks for feeding, drinking, and as access points for water entry.

Bank plants oiled during a flood period, especially if the flood rapidly subsides, could be susceptible to oil penetrating into bank sediments and contacting root systems. Small plants, particularly annuals, are likely to be most damaged. Stranded oil could remain in the habitat until another flood reaches the same level and provides a mechanism for natural flushing. On steep banks, the oil is likely to form a band, or multiple bands, at the waterline. On gentle banks, there is a greater potential for oil to accumulate in pools, penetrate the substrate, and coat large areas of vegetation, thus raising the issue of shoreline cleanup. In developed urban and suburban areas, human use and aesthetics would be the main reasons for cleanup.

Mud

Mud habitats are characterized by a substrate composed predominantly of silt and clay sediments, although they may be mixed with varying amounds of sand or gravel. The sediments are mostly water-saturated and have low bearing strength. In general, mud shorelines have a low gradient, although some steep banks also may consist of mud. The mud habitats generally are low energy and sheltered from wave action and high currents. Adjacent nearshore areas are usually shallow with muddy sediments. These fine-grained habitats often are associated with wetlands. Bare or sparsely vegetated mud substrates are rare along Great Lake shorelines. However, they commonly occur along river floodplains and lake bottoms, where they can be exposed during seasonal low water levels.

Mud habitats are highly sensitive to oil spills and subsequent response activities. Shoreline sediments are likely to be rich in organic matter and support an abundance of infauna. Muddy habitats are important feeding grounds for birds and rearing areas for fish.

Oil will not penetrate muddy sediments because of their low permeability and high water content, except through decaying root and stem holes or animal burrows. There can be high concentrations and pools of oil on the surface. Natural removal rates can be very slow, chronically exposing sensitive resources to the oil. The low bearing capacity of these shorelines means that response actions can easily leave long-lasting imprints, cause significant erosion, and mix the oil deeper into the sediments. When subsurface sediments are contaminated, oil will weather slowly and may persist for years. Response methods may be hampered by limited access, wide areas of shallow water, fringing vegetation, and soft substrate.

Wetlands

Wetlands are characterized by water, unique soils that differ from adjacent upland areas, and vegetation adapted to wet conditions. Wetlands include a range of habitats such as marshes, bogs, bottomland hardwood forests, fens, playas, prairie potholes, and swamps. Substrate, vegetation, hydrology, seasonality, and biological use of inland wetlands are highly variable, making characterization difficult. The surfaces of wetlands usually have a low gradient and vegetated areas are typically at, or under, the water level. There can be distinct channels or drainages with flowing water, except at the exposed outer-fringe; however, natural physical processes are minimal. Water levels may vary seasonally, and the wetland may be simply a zone of water-saturated soils during the dry season.

Wetlands are highly sensitive to oil spills. The biological diversity in these habitats is significant and they provide critical habitat for many types of animals and plants. Oil spills affect both the habitat (vegetation and sediments) and the organisms that directly and indirectly rely on the habitat. Surprisingly little is known about oil impact on freshwater plants, although there are likely differences between perennials that have substantial underground systems and cycles of winter die-back and annuals that do not. Detritus-based food webs are fundamentally important in wetlands; oil could possibly affect these by slowing decomposition rates of plant material.

Wetlands support populations of fish, amphibians, reptiles, birds, and mammals, with many species reliant upon wetlands for their reproduction and early life stages when they are most sensitive to oil. Many endangered animals and plants are found only in wetlands, and spills in such areas would be of particular conservation concern. Migratory waterbirds depend heavily on wetlands as summer breeding locations, migration stopovers, and winter habitats. The threat of direct oiling of animals using the wetland often drives efforts to remove the oil. If oil and/or cleanup efforts cause a loss of the more sensitive plants or modify the ecosystem structure, then feeding and breeding of dependent wildlife may be affected.

Section 3

CHARACTERISTICS OF OILS AND BEHAVIOR IN FRESHWATER

CRUDE OIL AND PETROLEUM PRODUCTS

The composition of crude oils and refined petroleum products varies greatly depending on their source and processing. Each oil is a complex mixture of hundreds of organic (and a few inorganic) compounds. These compounds differ in their solubility, toxicity, persistence, and other properties that profoundly affect their impact on the environment. Even the effects of spilled oil cannot be thoroughly understood without considering its specific composition. For this reason, this review of the fate and effects of oil spills in freshwater environments begins with a summary of the classes of compounds found in oils.

Components of Oils

The major classes of organic compounds in oils are alkanes (also called paraffins), cycloalkanes (also called naphthenes), and aromatics. Alkenes (olefins) are present in some refined oils. Most oils are about 95% carbon and hydrogen, with small amounts of sulfur, nitrogen, and oxygen, and traces of other elements. Petrov (1984) provides a detailed description of the hydrocarbons found in crude oils.

Alkanes. Alkanes (paraffins) consist of saturated carbon chains. All bonds between carbon atoms are single bonds, and all other binding sites are occupied by hydrogen. The two groups of alkanes in oils are normal alkanes (n-alkanes) and isoalkanes. Normal alkanes are simple, straight chains. Chain lengths of 5 to 10 carbon atoms (C_5 - C_{10}) are the most abundant in crude oils. Heptadecane (C_{17}) is a typical n-alkane. Iso-alkanes are branched carbon chains. Iso-alkanes containing 6 to 8 carbon atoms are the most abundant in most oils. Isooctane (2,2,4-trimethylpentane, C_8) is a typical iso-alkane. Olefins (or alkenes), which are found in refined gasoline, differ from alkanes in having one or more double bonds in the carbon chain.

Crude oils of terrestrial origin are typically rich in n-alkanes, while crude oils of marine origin contain more cycloalkanes. Crude oils that have biodegraded typically have lower amounts of n-alkanes because n-alkanes are easily degraded (Metcalf and Eddy, 1993).

Cycloalkanes. Cycloalkanes (naphthenes) are molecules containing saturated carbon rings. Typically, about half of the cycloalkanes in a crude oil contain one or two carbon rings, one quarter contain three rings, and one quarter contain four rings (Gill and Robotham, 1989). Cyclopentane (C_5) and cyclohexane (C_6) are common cycloalkanes found in many oils.

Aromatics. Aromatics contain one or more unsaturated carbon rings. They are of particular environmental significance because the lower molecular weight aromatics are more soluble in water than alkanes and cycloalkanes of similar weight, and because the higher molecular weight aromatics include many carcinogens. The lightest (and most soluble) aromatics are benzene, toluene (methyl benzene), ethyl benzenes, and xylenes (dimethyl benzenes), which together are commonly referred to as BTEX. Aromatics with two or more rings are called polyaromatic hydrocarbons (PAHs). Naphthalene, with two aromatic rings, is the simplest PAH. Anthracene (3 rings) and benz(a)pyrene (5 rings) are additional examples of PAHs.

Table 3-1 shows the concentrations of aromatics in two crude oils, No. 2 fuel oil and Bunker C residual oil (from Neff and Anderson, 1981). Benzenes make up more than 90% of the aromatics in the crude oils, 70% of the aromatics in No. 2 fuel oil, and 64% of the aromatics in Bunker C residual oil. The most abundant PAHs in all four oils are dimethylnaphthalenes. No. 2 fuel oil and Bunker C residual oil have more phenanthrenes and pyrene (3- and 4-ring aromatics) than the crudes. Bunker C residual oil has higher molecular weight PAHs than the other three oils.

Nitrogen, Sulfur, and Oxygen. Nitrogen-containing aromatics include pyrrole, pyridine, and quinoline (Gill and Robotham, 1989). Aromatics containing sulfur are called thiophenes, and make up about one-quarter of the aromatics in a typical crude oil (Gill and Robotham, 1989). Sulfur also may occur as elemental sulfur, hydrogen sulfide, and mercaptans (Metcalf and

Eddy, 1993). Oxygen is present in some aromatics (phenols), cycloalkanes (naphthenic acid), and fatty acids (Metcalf and Eddy, 1993).

Table 3-1. Concentrations of aromatics in two crude oils, No. 2 fuel oil, and Bunker C residual oil.

Compound	Concentration in mg/kg			
	Kuwait crude	South Louisiana crude	No. 2 fuel oil	Bunker C residual oil
Benzenes[a]	80000	92000	222000	60000
Naphthalene	400	400	4000	1000
1-methylnaphthalene	500	800	8200	2800
2-methylnaphthalene	700	900	18900	4700
Dimethylnaphthalenes	2000	3600	31100	12300
Trimethylnaphthalenes	1900	2400	18400	8800
Biphenyls	<100	<100	1600	<100
Fluorenes	<100	200	3600	2400
Phenanthrene	26	70	429	482
1-methylphenanthrene		111	173	43
2-methylphenanthrene	89	144	7677	828
Fluoranthene	2.9	5.0	37	240
Pyrene	4.5	3.5	41	23
Benz(a)anthracene	2.3	1.7	1.2	90
Chrysene	6.9	18	2.2	196
Triphenylene	2.8	10	1.4	31
Benzo(ghi)fluoranthene	<1	1		
Benzo(b)fluoranthene	<1	<0.5		
Benzo(j)fluoranthene	<1	<0.9		
Benzo(k)fluoranthene	<1	<1.3		
Benzo(a)pyrene	2.8	0.75	0.6	44
Benzo(e)pyrene	0.5	2.5	0.1	10
Perylene	<0.1	34.8		22
Benzo(ghi)perylene	<1	1.6		
Total aromatics analyzed	85637.7	100703.4	316162.5	94009

[a] Benzenes = benzene, alkylbenzenes, indans, tetralins and dinaphthenobenzenes

Source: Data from Neff and Anderson, 1981.

These nitrogen-, sulfur-, and oxygen-containing compounds (NSO compounds) are generally concentrated in the higher molecular weight, lower volatility fractions of oils (resins and asphaltenes). Resins and asphaltenes may comprise about 10% of a light paraffin oil, or as much as 60% of a heavily degraded crude oil (Gill and Robotham, 1989). Even though an oil may contain only a small fraction of NSO compounds, the compounds have a major influence on the oil's environmental behavior, as will be discussed below.

Table 3-2. Concentrations of metals in crude oils.

Element	Concentration (mg/kg) Minimum	 Maximum
Calcium	5,000	50,000
Aluminum	2,000	20,000
Magnesium	200	10,000
Titanium	100	5,000
Vanadium	2	1,200
Strontium	100	1,000
Barium	20	500
Nickel	2	200
Potassium	1	5
Sodium	3	20
Chlorine	2	39
Iron	1	125
Molybdenum	<1	10
Tin	<1	2
Zinc	0.67	63
Lead	0.17	0.31
Fluorine	0.14	1.1
Copper	0.13	6.3
Bromine	0.072	1.3
Manganese	0.05	11
Selenium	0.03	1.4
Antimony	0.03	0.15
Mercury	0.02	30
Rubidium	0.01	0.1
Gallium	0.01	0.3
Rhenium	<0.005	2.5
Gold	0.001	0.006
Cobalt	0.003	14
Arsenic	0.002	0.66
Europium	0.0005	0.002
Cesium	<0.0004	0.0004
Cadmium	0.0003	0.027
Scandium	0.0003	0.008
Chromium	0.0002	0.64
Uranium	0.00004	0.014

Source: From IARC, 1989; presented by Metcalf and Eddy, 1993.

Metals. Metals are present in oils in the form of inorganic salts, metallic soaps, and organometallic compounds. Calcium is typically the most abundant metal in crude oil, followed by aluminum and magnesium (Table 3-2).

Additives. Many petroleum products contain additives. For example, gasolines often contain antioxidants and oxygenating additives (e.g., methyl-tert-butyl-ether, MTBE). Lube oils may contain antioxidants, esters, copolymers, and organosilicones. Anti-sludging and anti-freezing agents sometimes are added to diesel and fuel oils (Gill and Robotham, 1989).

Classification of Oils

Crude oils. The composition of crude oils can vary, depending on the source organic material, geologic and thermal history, chemical changes during subsurface migration, biodegradation, oxidation, and dissolution. Tissot and Welte (1984) proposed the general classification of crude oils shown in Table 3-3. Most crude oils produced today are paraffin-naphthenic, aromatic intermediate, or paraffinic, whereas most reserves are aromatic asphaltic and aromatic naphthenic (Gill and Robotham, 1989).

Table 3-3. Classification of crude oils.

Classification	% Alkanes (paraffins)	% Cycloalkanes (naphthenes)	% Aromatics	Number of crudes
Paraffinic crude	40-90	10-40	0-40	100
Paraffin-naphthenic crude	10-40	10-40	20-50	217
Naphthenic crude	0-40	40-60	10-50	21
Aromatic intermediate crude	10-30	10-40	50-80	126
Aromatic-naphthenic crude	0-10	25-50	50-70	36
Aromatic asphaltic crude	0-10	10-25	70-90	41
		Total number of crudes classified		541

Source: From Tissot and Welte, 1984.

With such a broad range of crude oil composition, it may be an oversimplification to speak of an "average" crude oil. Nevertheless, for some purposes such a characterization may be useful. According to the National Academy of Sciences (NAS, 1975), an average crude oil contains 30% alkanes, 50% cycloalkanes, 15% aromatics, and 5% NSO compounds. The typical molecular size distribution is 30% C_5 - C_{10}, 10% C_{10} - C_{12}, 15% C_{12} - C_{20}, 25% C_{20} - C_{40}, and 20% $>C_{40}$.

Gasoline. The gasoline fraction of crude oil represents a boiling range of 80 to 150°C and consists mainly of C_5 - C_{10} alkanes (50%) and cycloalkanes (40%). Aromatics make up only about 10% of the gasoline fraction of crude oil. Blended gasoline containing catalytic cracking products has a much higher aromatic content (NAS, 1975). Regular gasoline contains about 50% aromatics, including 1 to 4% benzene and 3 to 20% toluene, as well as 15% n-alkanes, 30% isoalkanes, and 5 to 10% olefins (unsaturated carbon chains that are not commonly present in crude oil). Premium gasoline has slightly higher aromatic content (Müller, 1987). The aromatics in gasoline (mainly BTEX) are light, volatile, and relatively water-soluble. Gasoline contains less than 1% naphthalene and no PAH of three or more rings.

Kerosene. Kerosene has a boiling range of 150 to 250°C. Kerosene typically contains 35% alkanes, 50% cycloalkanes, and 15% aromatics. Most of the compounds are in the C_{10} to C_{12} range (NAS, 1975).

Diesel (No. 2 Fuel Oil). Diesel, also known as No. 2 fuel oil, has a boiling range of 250 to 300°C. It consists of C_{12} - C_{18} compounds, mainly C_{15} - C_{16}, and includes 30% alkanes, 45% cycloalkanes, and 25% aromatics (NAS, 1975). The aromatics include very little BTEX and higher proportions of PAH.

Bunker C Residual Oil (No. 6 Fuel Oil). Bunker C residual oil, also known as No. 6 fuel oil, is the heaviest distillate fraction of crude oil (>300°C) and consists mainly of C_{30} compounds and larger. These oils contain 15% alkanes, 45% cycloalkanes, 25% aromatics, and 15% NSO compounds (NAS, 1975).

Lube Oils. Lube oils have a boiling range of 450 to 500°C, and consist of C_{20} to C_{70} compounds. They contain more alkanes and cycloalkanes than aromatics. Commerical lube oils often contain a variety of additives (Gill and Robotham, 1989).

Asphalts. Asphalts are the very high boiling range (>500°C) residuals of crude oil. They are rich in high molecular weight aromatics and naphthenoaromatics (molecules containing both cycloalkane and aromatic rings). Most PAHs in asphalts contain seven or more rings (Metcalf and Eddy, 1993).

Synthetic oils. Synthetic petroleum substitutes may be derived from tar sands, oil shale, or coal. They are characteristically high in phenols and amines, compounds which are much more water soluble than typical petroleum hydrocarbons (Giddings *et al.*, 1985).

Characteristics of Oils

Besides its chemical composition, the properties of an oil that have the greatest influence on its physical behavior are its specific gravity (density), viscosity, and pour point. The specific gravity of an oil is the ratio of its density (mass per unit volume) to that of water at the same temperature. Oil density is often expressed as API Gravity (in units called degrees). API Gravity is calculated as follows:

$$\text{API Gravity(degrees)} = \frac{141.5}{\text{Specific Gravity}} - 131.5$$

Thus, an oil with a specific gravity of 1.0 (density equal to water) has an API Gravity of 10°. The more dense the oil, the lower its API Gravity. Most crude oils have a specific gravity between 0.79 and 1.00 (Clark and Brown, 1977). Representative densities of distillate fractions and one crude oil are presented in Table 3-4.

Viscosity is a measure of the resistance of a fluid to flow. A less viscous fluid flows more freely than a more viscous fluid. The viscosity of an oil increases as its temperature decreases; thus, oil may move more sluggishly when spilled into cold water or ice. Absolute viscosity is measured in units called poise (g/s·cm). Kinematic viscosity is the ratio of absolute viscosity to density, and is measured in units called stokes (cm/s^2). The viscosity of crude oils varies widely (Clark and Brown, 1977). Representative values for the viscosity of distillate fractions and a crude are presented in Table 3.4.

Table 3-4. Physical properties of oils.

Oil	Specific Gravity	API Gravity (degrees)	Viscosity (centipoise)	Pour Point (°C)
Gasoline	0.7	71	<1	
Kerosene	0.8	45	1-2	<-60
Diesel	0.82-0.85	35-40	40	-20
Bunker C	1	10	1,000	21
Prudhoe Bay crude	0.89	28	12	-10

Sources: NAS, 1975; Clark and Brown, 1977.

The pour point of an oil is the lowest temperature at which it can still be poured. Pour point is determined by gradually lowering the temperature while observing the oil in a glass container; the pour point is defined as the temperature 3°C higher than the temperature at which the oil surface no longer responds to tilting of the container. Pour points of crude oils can range from -43°C to 43°C (Clark and Brown, 1977). Pour points of some distillate fractions and a crude are shown in Table 3-4.

PROCESSES AFFECTING OIL IN FRESHWATER

The fate and behavior of an oil spilled in freshwater depend on the characteristics of the oil, the characteristics of the environment, and ambient conditions. For the most part, the processes influencing oil in freshwater are the same as those in marine environments. The following discussion incorporates information found in reviews of marine spills (NAS, 1975; Clark and MacLeod, 1977; Jordan and Payne, 1980).

Spreading and Drift

Spreading is an important process affecting an oil for the first six to ten hours after a spill (Jordan and Payne, 1980). Fay (1971) recommended formulae for calculating the spread of oil and described the underlying physical processes. Miyahara (1987) has described the spreading process. In calm water, spreading is controlled by three forces: gravity, viscosity, and surface tension. Immediately after a spill, gravity is the dominant force. The initial spreading rate is determined by the thickness of the slick and specific gravity of the oil (faster spreading with lower specific gravity). When the slick reaches a thickness of about 8 mm, further spreading is controlled by the oil's viscosity (faster spreading with lower viscosity). Eventually, surface forces become the controlling factor in spreading. Surface-active constituents (surfactants) are very important in this final stage of spreading. NSO compounds are significant surfactants in oils, as are many products of biological and chemical degradation (NAS, 1975).

The thickness of the slick decreases rapidly over time. Berridge *et al.* (1968) estimated that 100 m^3 of crude oil will reach a thickness of 55 mm in 17 minutes, 12 mm in 3 hours, and 3 mm in 28 hours. The final thickness of an oil slick can be much less than 1 μm. Ultimately, a monomolecular film is possible, but slicks are usually fragmented by wind and waves before this occurs. Thin oil films disappear rapidly: a 1-μm film may disappear within 24 hours, and a 0.01-μm film within 20 to 60 minutes (Miyahara, 1987).

As spreading proceeds, the surface area of oil in contact with air and water increases, enhancing the rates of evaporation and dissolution. Loss of the lighter oil constituents by evaporation and dissolution tends to increase the viscosity of the oil which, in turn, causes the spreading to slow down (Robotham and Gill, 1989). Most oils spread at rates of 100 to 300 meters per hour, though highly refined light oils (e.g., gasoline) may spread as rapidly as 600 meters per hour. Spreading is somewhat slower on freshwater than saltwater (Miyahara, 1987). Because the specific gravity, viscosity, and surface tension of both oil and water are temperature dependent, the rate of spreading increases by about 1.1% per degree C (Palczynski, 1987). The final dispersion area ranges from 1,000 to 40,000 m^2 per liter of oil (Miyahara, 1987).

Advection of oil by wind, waves, and currents is termed drift. The drift rate of a wind-driven oil slick is about 3 to 16% of wind speed (NAS, 1975; Robotham and Gill, 1989). In rivers and streams, drift with the current is usually the dominant mechanism. Under certain conditions, the wind can have a marked effect on the movement of oil on the water surface. Yapa *et al.* (1986; 1991a,b) developed models for surface drift of oil in rivers under various hydrodynamic conditions. Many models of spreading exist for the marine environment (Robotham and Gill, 1989) and may be applied (with modification) to large lakes.

Spreading and drift are strongly influenced by the presence of ice (Chen *et al.*, 1974, 1976). Spreading under ice is much slower than on open water, due to the physical resistance of the ice cover.

Emulsion and Dispersion

In the context of an oil spill, the term emulsification refers to incorporation of water droplets into oil, while dispersion refers to incorporation of oil droplets into the water. Emulsification prevails if the surface tension of the oil is less than that of the water, and dispersion prevails if the reverse is true (Miyahara, 1987). Mixing energy, such as the turbulence produced by waves in large lakes and waterfalls in rivers, is needed for either process to occur.

A water-in-oil emulsion is commonly called "mousse." Light oils (specific gravity <0.83) are unlikely to form mousse, while medium oils (specific gravity <0.9), crude oils rich in asphaltenes, and residual fuel oils form mousse readily if enough mixing energy is present. Mousse is more easily formed after volatile constituents have evaporated from the oil (Miyahara, 1987). The formation of mousse is enhanced by the presence of asphaltenes, waxes, and polar compounds including photodegradation and biodegradation products containing OH, CHO, OSO_3, and SO_3H functional groups (Mackay, 1987; Robotham and Gill, 1989).

Stable water-in-oil emulsions typically contain about 80% water and, therefore, occupy five times the volume of the original oil spilled. Emulsions containing droplets of uniform size (less than 5 µm) can be stable for a year or more. Emulsions with a heterogeneous droplet size distribution are less stable, because the droplets tend to coalesce (Miyahara, 1987). The viscosity of a mousse can be much greater than that of the original oil. Globs of mousse tend to become dispersed into the water and attach to objects. Eventually, pieces of mousse may solidify into tar balls (Mackay, 1987).

Oil-in-water dispersions are induced by turbulence from river currents, standing waves, waterfalls, riffles, etc. Dispersion is a principal factor affecting how long a slick will persist and how much will reach the shoreline (Mackay, 1987). Dispersibility is related to the viscosity and surfactant content of the oil. As with water-in-oil emulsions, NSO compounds act as surfactants and enhance dispersion of oil in water (Robotham and Gill, 1989).

Dispersion increases the surface area of the oil-water interface tremendously. Robotham and Gill (1989) estimated that one milliliter of oil can form 16×10^{12} droplets with a total surface area of 13 m^2. This large surface area results in increased rates of dissolution and biodegradation.

Oil-in-water dispersions are much less stable than water-in-oil emulsions. Hrudey and Kok (1987) discuss the physics of droplet behavior. Energy is needed to maintain the surface of a droplet; the smaller the droplet, the higher the surface area, and the more free energy is present in the interface per mass of oil. Surfactants, such as NSO compounds or chemical dispersants, reduce the surface tension of the droplets and, thus, reduce the energy needed to create and maintain the dispersion. Coalescence, by reducing the surface area, also reduces the energy content of the dispersion. Oil droplets may also aggregate (adhere to form clusters of droplets, without coalescing) or "cream" (collect at the water surface) (Hrudey and Kok, 1987).

Evaporation

Immediately after an oil is released on water, evaporation begins to remove the lighter components from the slick. Compounds $<C_{12}$ (including BTEX) evaporate within 8 hours, and compounds $<C_{15}$ within 10 days. There is no appreciable evaporative loss of compounds $>C_{25}$.

From 90 to 100% of a gasoline or kerosene will evaporate rapidly. For diesel, the volatile fraction is about 75%, and for Bunker C, less than 10%. Most crude oils will lose 30 to 50% by evaporation (NAS, 1975; Robotham and Gill, 1989).

Researchers have proposed several theories on the evaporation of oil. The more traditional views, discussed below, factor in temperature effects, spread, and wind and wave action. However, Fingas (1996) recently proposed that evaporation rate is linearly related to temperature change. A high correlation between distillation and evaporation was noted. This correlation led to the hypothesis that oil evaporation is governed primarily by intrinsic oil properties, rather than by environmental properties like boundary-layer factors.

Table 3-5. Vapor pressures and Henry's law constants (H) of oil constituents.

Compound	Vapor Pressure (Pa)[a]	H (dimensionless)[b]
n-pentane (C_5)	68,400	
n-heptane (C_7)	6,100	
n-decane (C_{10})	175	
n-dodecane (C_{12})	16	
benzene (C_6)	12,700	
p-xylene (C_8)	1170	
naphthalene (C_{10})	11	2.3×10^{-2}
phenanthrene (C_{14})	0.02	2.2×10^{-3}
anthracene (C_{14})	0.001	2.7×10^{-3}
pyrene (C_{16})	0.001	7.6×10^{-4}
benz(a)anthracene (C_{18})		3.3×10^{-4}
benz(a)pyrene (C_{20})		$<1 \times 10^{-4}$

[a] Source: Mackay, 1987.
[b] Source: Southworth, 1979.

The traditionalists, in contrast, assert that the tendency of a compound to evaporate is a function of its vapor pressure. Vapor pressures of representative oil constituents are presented in Table 3-5. Alkanes have the highest vapor pressures and, therefore, evaporate most quickly. Aromatics have lower vapor pressures than alkanes, and some NSOs (e.g., phenol) evaporate very slowly or not at all. Within a compound class, vapor pressure is inversely related to molecular weight. Thus, as evaporation proceeds, the composition of the remaining oil changes; for example, a crude oil begins to resemble Bunker C (NAS, 1975; Robotham and Gill, 1989). With the loss of the lighter components, the remaining oil becomes denser and more viscous (Table 3-6).

Table 3-6. Changes in properties of three oils due to evaporation.

Oil	Days Weathered[a]	Volume Remaining (%)	Specific Gravity (20°C)	Viscosity (cp) (20°C)
Norman Wells crude oil	0	100	0.832	4.41
	1	57	0.896	127.70
	3	56	0.897	130.30
	12	49	0.944	302.90
Alberta crude oil	0	100	0.836	5.22
	1	59	0.880	88.70
	3	57	0.900	190.60
	12	52	0.956	1,600.00
No. 2 Fuel Oil	0	100	0.862	3.64
	1	77	0.876	5.52
	3	65	0.878	6.88
	12	49	0.879	7.30

[a] Oils (initial film thickness 3 mm) were placed in a pan in a wind tunnel with wind speed approximately 5 m/s.
Source: Data from Shiu *et al.*, 1988.

As mentioned above, evaporation is enhanced by spreading of the oil slick. Evaporation is also accelerated by wind and waves. Wind and waves also lead to formation of aerosols, which under extreme conditions can transfer substantial amounts of whole oil (i.e., not just the volatile components) to the atmosphere. Evaporation is almost completely blocked if the oil occurs under a cover of ice.

Yang and Wang (1977) modeled the evaporative loss from a crude oil spill and a spill of No. 2 fuel oil. Their model and experimental data indicated that temperature and wind speed affected the rate of evaporation. They reported model results showing that 40% of the No. 2 fuel oil evaporated within the first 50 hours at 14°C with a wind speed of 3.2 m/s. Bobra (1992) showed that from 40% to more than 80% of diesel oil and 20% to 35% of North Slope crude evaporated within 10 days, depending on the thickness of the slick (0.1 mm to 15 mm).

Evaporation can affect oil constituents that are dissolved in the water as well as those in the slick. The tendency for a compound to volatilize from water is directly proportional to its Henry's law constant (H), derived from the ratio of its vapor pressure to its water solubility. Henry's law constants for representative oil constituents are presented in Table 3-5. H increases with increasing temperature. Evaporation from water is accelerated by water turbulence. Compounds with $H > 0.1$ (e.g., benzene and toluene) evaporate from turbulent waters with half-lives in the range of 1 to 2 hours (Müller, 1987). Half-lives for less volatile compounds may be much longer; for example, 20 to 300 days for benz(a)pyrene, depending on wind and current (Southworth, 1979). Anderson *et al.* (1974) determined that oil-in-water dispersions of two crude oils and No. 2 fuel oil lost 81 to 97% of their n-paraffins and 52 to 79% of their aromatics after 24 hours of gentle aeration in the laboratory.

Dissolution

Most components of oils are relatively insoluble in water (see Table 3-7). The bulk loss of crude oil by dissolution is about 1 to 3%, compared to 10 to 40% or more for evaporation and dispersion (Mackay, 1987). Dissolution is, therefore, much less important than evaporation in determining the fate of spilled oil. However, in a confined body of water, the small fraction of oil that does dissolve may be responsible for much of the toxic impact of a spill. The composition and toxicity of the water soluble fractions (WSFs) of oils, therefore, have received a great deal of attention from researchers.

Table 3-7. Solubility and octanol-water partition coefficients (K_{ow}) of oil constituents.

Compound	Solubility mg/L	µmole/L	log K_{ow}
	Alkanes (Paraffins)		
hexane	9.5	110	3.00
3-methylpentane	12.8	149	2.80
octane	0.66	5.7	4.00
decane	0.052	0.365	5.01
dodecane	0.0038	0.0222	6.10
tetradecane	0.0023	0.0115	7.20
	Cycloalkanes (Naphthenes)		
cyclopentane	156	2224	2.05
cyclohexane	55	654	2.44
methylcyclopentane	42	499	2.35
methylcyclohexane	14	143	2.76
cyclooctane	7.9	70	3.28
	Aromatics		
benzene	1780	22790	2.13
toluene	515	5589	2.69
ethylbenzene	152	1432	3.08
p-xylene	185	1742	3.15
p-ethyltoluene	95	780	3.63
o-ethyltoluene	93	774	3.63
naphthalene	31.7	247	3.35
1-methylnaphthalene	28.5	200	3.86
2-methylnaphthalene	25.4	178	3.86
biphenyl	7.0	45	4.02
phenanthrene	1.29	7.2	4.63
anthracene	0.042	0.23	4.63
pyrene	0.135	0.67	5.22
1,2-benzanthracene	0.014	0.0613	5.91
chrysene	0.0019	0.00876	5.79
benzo(a)pyrene	0.0038	0.015	5.98
perylene	0.00040	0.0016	6.50
benzo(ghi)perylene	0.00026	0.00094	7.10
coronene	0.00014	0.00047	7.64

Source: Hutchinson *et al.*, 1980, except 1,2-benzanthracene, chrysene, benzo(a)pyrene, perylene, benzo(ghi)perylene, and coronene from Miller *et al.*, 1985. Taken from Müller, 1987.

Among molecules of similar molecular weight, alkanes are the least soluble and aromatics are the most soluble. This trend is observed, for example, in a comparison of the solubility of hexane (9.5 mg/L), cyclohexane (55 mg/L), and benzene (1780 mg/L). Within each group of compounds, solubility decreases with increasing molecular weight. In most cases, isomers (e.g., o- and p-ethyltoluene, or 1- and 2-methylnaphthylene) have similar solubilities; anthracene and phenanthrene are notable exceptions. Generally, NSO compounds in oil are not more soluble than aromatics of similar molecular weight (NAS, 1975). However, products of photochemical or biological oxidation tend to be more polar and, therefore, more water-soluble than the parent compounds. For example, the solubility of naphthalene is 32 mg/L, while that of its oxidation product α-naphthol is 740 mg/L (NAS, 1975).

Solubility is a function of temperature, salinity, and dissolved organic matter concentration. Solubility increases with increasing temperature; for example, the solubility of anthracene in distilled water is 12.7 µg/L at 5.2°C and 55.7 µg/L at 28.7°C (May *et al.*, 1978). Solubility decreases with increasing salinity. The solubilities of methylcyclohexane and methylnaphthalene are each about 15% lower at 14 $^0/_{00}$ salinity (about half of natural seawater) than in deionized water (Burris and McIntyre, 1987), and solubilities of hydrocarbons in full-strength seawater may be as much as 30% lower than in freshwater (Rossi and Thomas, 1981; NAS, 1975). Dissolved organic matter increases the apparent solubility of aromatics (McCarthy and Jimenez, 1985a).

The overall solubilities of oils are consistent with the solubilities of their individual constituents. Heavier oils generally are less soluble than lighter oils (Tables 3-8 and 3-9). The relationships among solubility, temperature, and salinity apply to whole oils as well as individual compounds (Table 3-8). However, although the trends observed for pure compounds are valid for whole oils, the overall solubility of an oil is not very useful in an ecological risk assessment. The actual concentrations of oil components in water beneath a slick are controlled not by the solubility limits of those components in water, but by the partitioning between the oil and water phases. Because the individual compounds are much more soluble in oil than in water, they tend to remain in the oil, and the amounts that enter the water are much less than the aqueous solubility limits (see Table 3-10). Toxicity of oil constituents in the aquatic environment is related to two inversely related factors: the individual compound's potency and its water solubility. In general, hydrophobic compounds are inherently more toxic per unit compound than water-soluble compounds. Nevertheless, the toxicity of hydrophobic compounds in aquatic systems is limited since only a relatively small amount is dissolved in water. Alternatively, water-soluble compounds tend to be less toxic per unit of compound compared to hydrophobic compounds. Nevertheless, more of the compound is present in the water column due to increased water solubility. When oil is released into the environment, water soluble compounds are primarily responsible for observed acute toxicity due to differential solubility and potency of the individual constituents. Because the overall solubility of oil decreases with salinity, the toxicity of oil in freshwater is expected to be slightly greater than in seawater. The implications of differential solubility and toxicity for toxicity testing and risk assessment will be discussed in Section 4.

Table 3-8. Solubility of crude oils as a function of specific gravity (API °), temperature, and salinity (distilled water vs. seawater).

API Gravity (°)	Distilled Water			Seawater (44 $^0/_{00}$)		
	25°C	35°C	45°C	25°C	35°C	45°C
11	3.5	4.5	6.0	2.5	4.0	5.5
15	4.0	5.0	7.0	3.0	4.5	6.0
20	10.0	14.0	18.0	8.5	12.0	15.0
28	65.0	75.0	90.0	55.0	61.0	70.0

Values are mg/L total dissolved oil, measured using a Horiba Model OCMA-200 oil analyzer.
Source: Hamam *et al.*, 1988.

Table 3-9. Solubility of oils in freshwater.

Oil	API Gravity (°)	Solubility (mg/L)
Gasoline	60 - 62.4	169 - 306
Jet Fuel (A-1)	44.8 - 56.7	8.73
Diesel (No. 2 Fuel Oil)	39.4	2.8 - 3.12
South Louisiana Crude	34.5 - 37	37.9
Alaska North Slope Crude	26.4	27.98
Virgin Lube Oil	29	0.2 - 0.99
Bunker C (No. 6 Residual Oil)	7.3 - 14	4.45

Source: Bobra, 1992.

Table 3-10. Concentrations of oil constituents in water-soluble fractions of four oils.

Compound	Kuwait crude oil	South Louisiana crude oil	No. 2 fuel oil	Bunker C residual oil
Alkanes				
ethane	0.23	0.54	0.39	0.05
propane	3.30	3.01		
butane	3.66	2.36		
isobutane	0.90	1.69		
pentane	1.31	0.49		
isopentane	0.98	0.70		
cyclopentane + 2-methylpentane	0.59	0.38	0.02	0.005
methylcyclopentane	0.19	0.23	0.019	0.004
hexane	0.29	0.09	0.014	0.004
methylcyclohexane	0.08	0.22	0.03	0.002
heptane	0.09	0.06	0.02	0.004
total C_{12} - C_{24} n-paraffins	0.004	0.089	0.047	0.012
Total saturates	11.62	9.86	0.56	0.081
Aromatics				
benzene	3.36	6.75	0.55	0.04
toluene	3.62	4.13	1.04	0.08
ethylbenzene + xylenes	2.25	5.96	1.27	0.12
trimethylbenzenes	0.73	0.76	0.97	0.11
naphthalene	0.02	0.12	0.84	0.21
1-methylnaphthalene	0.02	0.06	0.34	0.19
2-methylnaphthalene	0.008	0.05	0.48	0.20
dimethylnaphthalenes	0.02	0.06	0.24	0.20
trimethylnaphthylenes	0.003	0.008	0.03	0.10
biphenyl	0.001	0.001	0.011	0.001
methylbiphenyls	0.001	0.001	0.014	0.001
dimethylbiphenyls	0.001	0.001	0.003	0.001
fluorene	0.001	0.001	0.009	0.005
methylfluorenes	0.001	0.001	0.009	0.004
dimethylfluorenes	0.001	0.001	0.002	0.002
dibenzothiophene	0.001	0.001	0.004	0.001
phenanthrene	0.001	0.001	0.010	0.009
methylphenanthrenes	0.001	0.002	0.007	0.011
dimethylphenanthrenes	0.001	0.001	0.003	0.003
Total aromatics	10.04	13.91	5.83	1.288
Total dissolved hydrocarbons measured	21.66	23.77	6.39	1.369

Values are mg/L.

Source: Anderson *et al.*, 1974. Taken from Neff and Anderson, 1981.

Sorption, Sedimentation, and Sinking

Clark and MacLeod (1977) list five weathering processes that together lead to the sinking of oil and oil components: (1) evaporation and dissolution, which remove low molecular weight components; (2) degradation and oxidation; (3) formation and agglomeration of dispersed particles; (4) sorption to particulate matter; and (5) emulsification. Evaporation, dissolution, degradation, dispersion, and emulsification are discussed in other sections of this review.

The tendency for an individual compound to sorb to particles is quantified by its partition coefficient, K_p, which is the ratio of sorbed compound per mass of particles to dissolved compound per volume of water. The value of K_p for a compound varies depending on the properties of the particles, especially their organic content. The organic partitioning coefficient, K_{oc}, is a constant for a given compound. For particles whose organic content (F_{oc}) is greater than 0.1%, $K_p = K_{oc} \times F_{oc}$ (Karickhoff *et al.*, 1979). K_{oc} is closely correlated with the octanol-water partition coefficient (K_{ow}), a physical-chemical constant whose value has been measured for a great number of organic molecules (Karickhoff *et al.*, 1979; Means *et al.*, 1980). The relative tendency of oil constituents to bind to particles can, therefore, be determined by examination of their K_{ow} values (Table 3-7).

Sorption of organic compounds to particles is thought to be mainly due to the coating of organic matter on the particle surface. McCarthy and Jimenez (1985a) and others have shown that PAHs are sorbed to dissolved organic matter (DOM) in the same way that they are sorbed to particles. In waters rich in humic acids ("brown waters"), the amount of PAHs sorbed to DOM may be greater than the amount sorbed to particles.

Dissolved oil constituents can bind to inorganic particles, especially clays (Green and Trett, 1989). This process is mediated by ionic forces, which are much stronger in seawater than freshwater. Although salts in seawater enhance binding, freshwater contains a greater number of particles for binding (Green and Trett, 1989). Flocculation of organic and inorganic material contributes to particle formation and sedimentation of oil in seawater, but is not a significant mechanism in freshwater (Clark and MacLeod, 1977; Robotham and Gill, 1989; Green and Trett, 1989).

Sorption of oil constituents to particles and dissolved organic matter makes them less available to organisms (Landrum and Scavia, 1983; Leversee *et al.*, 1983; McCarthy, 1983; McCarthy and Jimenez, 1985b). Sorbed organics are also less susceptible to biodegradation (Robotham and Gill, 1989) and photooxidation (Zepp and Schlotzhauer, 1979).

Suspended particles can become coated with whole oil and can become incorporated into whole oil through the formation of water-in-oil emulsions (Clark and MacLeod, 1977). As mousse becomes increasingly dense and viscous, it is likely to sink to the bottom where it can pick up sediment particles as well as stones, shells, and other objects. Continued weathering leads to the formation of tar balls, enriched in asphaltenes and NSO compounds, and containing inorganic particles as well as liquid oil. Tar balls can be transported by currents and eventually deposited on the shoreline.

In some cases, oil does not sink to the bottom but remains in a neutrally buoyant state. This phenomenon is especially likely to occur in estuaries, where freshwater (lower density) overlies saltwater (higher density). Oil masses may become heavier than the surface water and sink until reaching the denser water below, where they are neutrally buoyant and can be transported long distances by subsurface currents. For example, in the *Presidente Rivera* spill (Wiltshire and Corcoran, 1991), a high pour point No. 6 residual oil sank in the cold waters of the Delaware River, only to reappear at the surface of the river and on shorelines downstream.

Oil and oil constituents that reach the sediment or shoreline may persist over time scales ranging from a few days to decades (Baker, 1997). The dominant factor appears to be shore exposure to wave energy. On hard bottoms and high-energy rocky shorelines, oil persists mainly localized in crevices and pores (Clark and MacLeod, 1977). In fine-grained sediments and low-energy shorelines, oxygen depletion can retard oil degradation. Contaminated sediment can become covered with clean deposits, only to be uncovered years later during storms.

Photodegradation

Under ultraviolet (UV) and near-UV light, oil constituents can be oxidized to form carboxylic acids, alcohols, peroxides, ethers, and a variety of other products (see reviews by Clark and MacLeod, 1977; Payne and Phillips, 1985; Robotham and Gill, 1989). In general, the photodegradation products are more soluble in water than the parent compounds. However, in a thicker oil layer, the degradation products may accumulate and form a viscous skin on the upper surface (Klein and Pilpel, 1974). The "gum" that forms in degraded gasoline consists of peroxides created by oxidation of olefins (Clark and MacLeod, 1977).

Some oil constituents act as photosensitizers, increasing the rate of photodegradation of other components. Examples include 1-naphthol, fluorenone, perylene, and certain metallo-organics (Larson *et al.*, 1977; Patel *et al.*, 1979; Clark and MacLeod, 1977). Humic acids found in natural waters also can be photosensitizers. Other oil constituents, particular sulfur-containing compounds, inhibit photooxidation. Crude oils with high sulfur contents, therefore, are less susceptible to photodegradation, while removal of sulfur during refining may make refined products more susceptible (Robotham and Gill, 1989). Herbes and Whitley (1983) found that diesel oil photodegraded faster than synthetic fuels, while the crude oils they tested did not photodegrade at all.

Payne and Phillips (1985) conclude that photodegradation in oil slicks can occur at rates comparable to evaporation and faster than biodegradation. Photodegradation may lead to disappearance of an oil film within a few days (NAS, 1975). Mousse degrades much more slowly due to its reduced surface area (Clark and MacLeod, 1977). Aromatics dissolved in the water photodegrade in full sunlight (i.e., near the water surface at midday in summer) with half-lives ranging from less than one hour for anthracene, pyrene, and benzapyrene to 71 hours for naphthalene (Zepp and Schlotzhauer, 1979). PAH photolysis is slower in turbid water due to reduced light transmission and sorption of the aromatics to particles.

Photodegradation has been shown to increase the toxicity of oils to aquatic organisms. Lacaze and Villedon de Naïde (1976) found that the toxicity of Kuwait crude to algae increased in the light. Larson *et al.* (1977) measured an increase in toxicity of No. 2 fuel oil to baker's yeast (not a typical inhabitant of aquatic ecosystems, but indicative of effects on natural biota). Herbes and Whitley (1983) showed that photoproducts of synthetic fuels were more toxic than the original oils to *Daphnia magna*. These increases in toxicity probably are due mainly to the increase in solubility (higher concentrations of organics in the WSF) and, in part, to the formation of more toxic oxidation products.

Biodegradation

Hydrocarbon-degrading microorganisms (bacteria, yeasts, and filamentous fungi) are ubiquitous in natural water and sediment, but are not abundant in areas that have not experienced petroleum contamination (Clark and MacLeod, 1977; Herbes and Schwall, 1978; Foght and Westlake, 1987). Areas affected by spills or by chronic oil contamination develop much higher populations of oil degraders (Horowitz and Atlas, 1977). Some of these organisms derive energy from degradation of oil constituents, while others degrade petroleum hydrocarbons incidentally while consuming other organic substrates (co-metabolism).

In general, n-alkanes degrade faster than isoalkanes, cycloalkanes, or aromatics. Asphaltenes and NSOs are the least degradable oil constituents (Foght and Westlake, 1987). Low molecular weight n-alkanes, mono- and diaromatics, and some cycloalkanes can be mineralized to CO_2 by some microorganisms, including the bacterial genera *Pseudomonas*, *Flavobacterium*, and *Chromobacterium* (Foght and Westlake, 1987; Trzilová and Miklošovicová, 1990). Some low molecular weight compounds, such as short n-alkanes, benzene, and toluene, are toxic to some microbial species, and biodegradation rates may increase as these compounds are removed from the oil by evaporation and dissolution. Higher molecular weight n-alkanes and PAH are more resistant to biodegradation, but may be partially degraded (Müller, 1987). Partially degraded products from one species may be further metabolized by other species; thus, mixed populations of microorganisms are usually more effective at degrading oils than single strains (Müller, 1987). Partial degradation can also lead to formation of less degradable, high molecular weight products (Walker and Colwell, 1976a; Horowitz and Atlas, 1977).

Because bacteria tend to concentrate at the oil-water interface, dispersed oil droplets tend to biodegrade more quickly than larger masses of oil (Foght and Westlake, 1987). Some bacteria produce surfactants which increase the oil surface area. Chemical dispersants may increase the degradation rate by increasing the oil surface area or may inhibit degradation through a toxic influence on the bacteria (Foght and Westlake, 1987). Formation of mousse and tarballs reduces surface area and decreases the biodegradation rate.

Biodegradation of oil requires oxygen and nutrients, especially nitrogen and phosphorus. Zobell (1964, cited by Müller, 1987) estimated that oxidation of 1 mg of oil required 3 to 4 mg of oxygen, and that complete biodegradation of 1 L of oil would, therefore, consume all of the oxygen (assuming 8 mg/L in oxygen-saturated water) in 400 m^3 of water. In quiet freshwater environments, and especially in sediments, biodegradation of oil can result in depletion of dissolved oxygen (Franco *et al.*, 1984; Giddings *et al.*, 1984; Robotham and Gill, 1989). Under low oxygen or anaerobic conditions, hydrocarbon biodegradation proceeds very slowly (Müller, 1987; Foght and Westlake, 1987). Aeration (Trzilová and Miklošovicová, 1990) and nutrient enrichment (Foght and Westlake, 1987) can accelerate biodegradation of oils. In freshwater ecosystems, nutrient concentrations are typically highest in winter and spring and lowest in midsummer. Nutrient enrichment can occur through inputs of agricultural runoff and domestic sewage, or through deliberate additions for oil spill remediation.

Rates of biodegradation are somewhat dependent on temperature. Depending on the oil, degradation at 20°C may be from one-third to four times faster than at 10°C (Atlas, 1975). In addition to the influence of temperature on microbial metabolism, higher temperatures can reduce oil viscosity, thereby enhancing dispersion and increasing the area of the oil-water interface (Clark and MacLeod, 1977).

Photooxidation may result in formation of polar compounds which are more soluble and therefore more amenable to biodegradation. Sorption to particles makes oil hydrocarbons less available for biodegradation.

SUMMARY

The behavior and fate of spilled oil products in freshwater systems are controlled by several interacting chemical and environmental factors. Certain processes that act to decrease the physical quantity of oil present may, at the same time, increase the potential for adverse effects to aquatic species as well as the persistence of remaining constituents. Behavior of oil in the environment varies dramatically with the type of product and its chemical composition. The oil's physical and chemical properties will control both its susceptibility to degradation and its tendency to disperse in the environment.

Seven primary processes were discussed as affecting the fate and behavior of spilled oil in water:

- spreading and drift;
- emulsification and dispersion;
- evaporation;
- dissolution;
- sorption, sedimentation, and sinking;
- photodegradation; and
- biodegradation.

As each of these processes occurs, the quantity of oil within the immediate vicinity of a spill will be reduced. However, each also will cause changes in the chemical and physical properties of oil remaining.

In general, lighter molecular weight constituents and lighter, more refined, products will be more susceptible to the fate processes listed. The lighter oils and oil constituents will tend to remain in the environment for a shorter time. As discussed in the next chapter, these products also tend to be more toxic to aquatic species than the heavier oils.

The fate and behavior of oil in freshwater systems are, in large part, controlled by the dynamics of the particular system into which a spill occurs. Oil will tend to spread and dissolve faster in flowing systems than in static ones. Dissolved constituents will tend to cause greater effects in smaller confined systems, and persistent products may remain for very long time periods in such water bodies.

Spreading of oil increases with decreasing oil density and increasing temperature. Most oil products spread at a rate of 100-300 m/hr, with some highly refined products reaching rates of 600 m/hr. Spreading reduces the bulk quantity of oil present in the vicinity of the spill but increases the spatial area within which adverse effects may occur. Oil in flowing, as opposed to contained, systems will be less concentrated in any given location, but may cause impacts, albeit reduced in intensity, over a much larger area. Spreading and thinning of spilled oil increase the surface area of the slick, thus enhancing surface-dependent fate processes such as evaporation, degradation, and dissolution.

Emulsification and dispersion of oil increase with increasing surface turbulence. Water-in-oil emulsions can be highly persistent and resistant to degradation processes. They may cause severe habitat effects due to precipitation of oil along shorelines and attachment to objects. The dispersion of oil into water, in contrast, may serve to increase the surface area of oil susceptible to dissolution and degradation processes and, thereby, limit the potential for physical impacts.

Evaporation will be the primary mechanism of loss for low molecular weight constituents and light oil products. As lighter components evaporate, the remaining oil becomes denser and more viscous. Evaporation, thus, tends to reduce oil toxicity but enhance oil persistence of the remaining oil. Bulk evaporation typically ranges from 10% to 40% but may be much higher for some products (e.g., 90 to 100% for gasoline). Research has indicated that evaporation increases with increased spreading of a slick, increased temperature, and increased wind and wave action. A recent study, however, suggests that evaporation is linearly related to temperature change; intrinsic oil properties dominate and environmental properties like boundary-layer factors have a minimal effect on evaporation.

Dissolution of oil in water is not a significant process controlling the oil's fate in the environment. However, it is one of the primary processes affecting the toxic effects of a spill, especially in confined water bodies. Dissolution increases with decreasing molecular weight, increasing temperature, decreasing salinity, and increasing concentrations of dissolved organic matter.

Sorption of spilled oil to suspended particulates can be significant in highly turbid waters. Organic particles (e.g., biogenic material) tend to be more effective at sorbing oil than inorganic particles (e.g., clays). Sorption and sedimentation reduce the quantity of oil present in the water column and available to aquatic organisms. However, these processes also render the oil less susceptible to degradation. Sedimented oil tends to be highly persistent and can cause undesirable shoreline impacts.

Photodegradation of oil increases with greater solar intensity. It can be a significant factor controlling the disappearance of a slick, especially of lighter products and constituents; but, it will be less important during cloudy days and winter months. Greater photodegradation also tends to enhance the solubility of oil in water. Photodegraded oil constituents can be more soluble and more toxic than parent compounds. Extensive photodegradation, like dissolution, may increase the biological impacts of a spill.

Natural biodegradation of oil will not tend to be a significant process controlling the fate of spilled oil in water bodies previously unexposed to oil, at least not within the immediate aftermath of a spill. Microbial populations must become established before biodegradation can proceed at any appreciable rate. Prior to weathering (i.e., evaporation and dissolution of light-end constituents), oils may be toxic to the very organisms responsible for biodegradation. High molecular weight constituents, emulsions, and tarballs tend to be resistant to biodegradation. The process is enhanced as the surface area of spilled product increases (e.g., by dispersion or spreading). Biodegradation is nutrient and oxygen demanding and may be precluded in low nutrient (oligotrophic) systems. It may also deplete oxygen reserves in closed water bodies, causing adverse secondary effects to aquatic organisms.

Section 4

ECOLOGICAL EFFECTS OF SPILLED OIL IN FRESHWATER ENVIRONMENTS

Ecological effects resulting from oil spills into freshwater systems are as diverse as the various types of habitats included within this section and the types of petroleum products potentially spilled. The magnitude and types of effects that may occur will depend on such factors as the hydrologic dynamics of the impacted water body, its chemistry, the species assemblages present, season, petroleum product chemistry, spill response tactics employed, and so on. A number of laboratory and field-observational investigations have evaluated the toxicological and ecological effects of petroleum products on freshwater organisms, and these are reviewed in this section. Unfortunately, experimental methods vary widely, making it difficult to synthesize available information. Nonetheless, certain patterns and conclusions are evident from the literature, and these are presented in the sub-sections that follow. Work remains to be done in an effort to standardize laboratory testing and field investigation methods, so that valid and valuable comparisons can be drawn between oil effects data sets.

This section is divided into two parts. The first focuses on reported toxicity values for oil constituents; the second focuses on the effects of oils on freshwater organisms. Response data are summarized for many types of organisms exposed to numerous petroleum-based compounds. Where applicable, generalizations as to evident trends in the data are provided. Testing methods are described, and the effect on response variables of the methods with which oil is introduced into test systems is reviewed. Those fractions of petroleum products primarily responsible for oil toxicity (the light end compounds) are identified, providing important information regarding the relative toxicities of freshly spilled, versus weathered, oils. The results suggest that the toxicity of an oil is generally predictable from its chemical composition. The reader is cautioned, however, that results comparisons between different investigations are often inappropriate due to significant variances in experimental methods and reporting strategies.

The second part of the section summarizes published accounts of potential effects of oils on freshwater fish, plants, algae, invertebrates, microorganisms, amphibians and reptiles, and birds and mammals. The discussion is segregated by organism group and response type. The reader is referred to other comprehensive effects reviews available in the literature. Where appropriate, ecological implications for cleanup response strategies are discussed.

Freshwater oil spills may severely impact organism assemblages, and several studies have documented major post-spill plant and animal losses. Unfortunately, the quantity of information specific to freshwater systems is limited in comparison to that discussing the ecological and toxicological effects of marine oil spills. It is hoped that this review will draw attention to the need for additional study of the impact of oil spills on freshwater systems, while at the same time providing some practical information on the subject.

TOXICITY OF OIL CONSTITUENTS

Within a class of petroleum hydrocarbons, toxicity to aquatic organisms generally increases, with increasing molecular weight, alkyl substitution, or carbon ring number, to a limit based on water solubility. This trend has been observed with bacteria (Bringmann and Kühn, 1980), algae (Giddings, 1979; Hutchinson *et al.*, 1980; Bringmann and Kühn, 1980; Coffey *et al.*, 1977; Millemann *et al.*, 1984a), protozoa (Bringmann and Kühn, 1980; Rogerson *et al.*, 1983), daphnids (Bringman and Kühn, 1977; Bobra *et al.*, 1983a; Trucco *et al.*, 1983; Millemann *et al.*, 1984a), mosquito larvae (Berry and Brammer, 1977), and other freshwater species (Millemann *et al.*, 1984a). Examples are presented in Tables 4-1 through 4-4.

Acute toxicity data are typically presented as LC_{50} values. The LC_{50}, or median lethal concentration, is the concentration of a material estimated to cause 50% mortality. The more toxic the material, the lower its LC_{50}. Other measures of toxicity, such as No-Observed Effect Concentrations (highest concentrations that cause no statistically significant effect [NOEC]) or subjective toxicity thresholds (e.g., Table 4-4), are reported by some researchers.

Table 4-1. Acute toxicity of petroleum hydrocarbons to *Daphnia magna* (zooplankton).

Compound	48-h LC_{50} (mg/L)	Solubility (mg/L)	LC_{50}/Solubility
Alkanes			
pentane	9.7	39	0.25
hexane	3.9	9.5	0.41
octane	0.37	0.66	0.57
decane	0.028	0.052	0.57
Cycloalkanes			
cyclopentane	10.5	156	0.07
cyclohexane	3.8	55	0.07
methyl cyclohexane	1.5	14	0.11
Monoaromatics			
benzene	31.2	1780	0.02
toluene	11.5	515	0.02
ethylbenzene	2.1	152	0.01
p-xylene	8.5	185	0.05
m-xylene	9.6	162	0.06
o-xylene	3.2	175	0.02
1,2,4-trimethylbenzene	3.6	57	0.06
1,3,5-trimethylbenzene	6.0	97	0.06
cumene	0.60	50	0.01
1,2,4,5-tetramethylbenzene	0.47	3.5	0.14
Polyaromatics			
naphthalene	17	121[a]	0.14
1-methylnaphthalene	1.4	28	0.05
2-methylnaphthalene	1.8	32[a]	0.06
biphenyl	3.1	21[a]	0.15
phenanthrene	1.2	6.6[a]	0.18
anthracene	3.0	5.9[a]	0.52
9-methylanthracene	0.44	0.88[a]	0.50
pyrene	1.8	2.8[a]	0.64

Source: From Bobra *et al.*, 1983a.

[a] Estimated subcooled liquid solubility, using fugacity ratio (higher than solid solubility)

Table 4-2. Acute toxicity of five aromatic compounds to *Daphnia pulex* (zooplankton).

Compound	96-h LC_{50} (μg/L)
benzene	15,000
naphthalene	1,000
phenanthrene	100
benzo(a)anthracene	10
benzo(a)pyrene	5

Source: From Trucco *et al.*, 1983.

Table 4-3. Acute toxicity of six petroleum constituents to aquatic organisms.

	LC_{50} (mg/L)					
Species	naphthalene	Phenanthrene	phenol	β-naphthol	quinoline	acridine
Rainbow trout[a]	0.12	0.03	0.12	0.07	11.5	0.30
Largemouth bass[b]	0.68	0.25	2.67	1.00	7.42	0.91
Fathead minnow[c]	1.99	[f]	25.6	3.46	0.44	2.24
Daphnia magna[d]	2.16	0.70	19.8	3.54	34.5	2.05
Chironomus tentans[d]	2.81	0.49	105	4.32	56.8	1.86
Gammarus minus[d]	3.93	0.46	37.4	0.85	40.9	1.87
Nitzschia palea[e]	2.82	0.87	185	6.31	104	20.8
Selenastrum capricornutum[e]	2.96	0.94	287	18.8	202	20.0
Physa gyrina[d]	5.02	[f]	260	24.7	183	11

Source: From Millemann *et al.*, 1984a.

[a] 27-d exposure; eggs and larvae

[b] 7-d exposure; eggs and larvae

[c] 96-h exposure; juveniles

[d] 48-h exposure

[e] 4-h exposure

[f] LC_{50}s could not be calculated

Table 4-4. Acute toxicity of petroleum constituents to *Pseudomonas putida* (bacteria), *Scenedesmus quadricuada* (algae), and *Entosiphon sulcatum* (protozoa).

	Toxicity Threshold (mg/L)		
Compound	Bacteria	Algae	Protozoa
Monoaromatics			
benzene	92	>1,400	>700
toluene	29	>400	456
ethylbenzene	12	>160	140
2-methylfurane	90	40	107
1,2-diethylbenzene	>20	>20	6.9
styrene	72	>200	>256
Phenols			
phenol	64	7.5	33
o-cresol	33	11	17
m-cresol	53	15	31
hydroquinone	58	0.93	11
Nitrogen compounds			
cyclohexyl amine	420	0.51	0.7
aniline	130	8.3	24
o-toluidine	16	6.3	76
nitrobenzene	7	33	1.9
pyridine	340	120	3.5

Source: From Bringmann and Kühn, 1980.

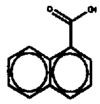
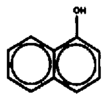
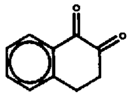
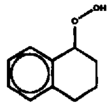
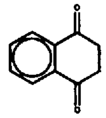
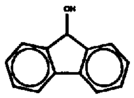
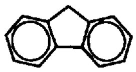
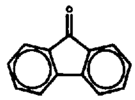
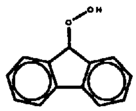
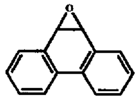
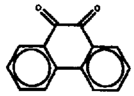
Like toxicity, aqueous solubility and octanol-water partition coefficients (K_{ow}) show consistent trends with increasing molecular weight, alkyl substitution, and carbon ring number. Bobra *et al.* (1983a) explained the trends in toxicity on the basis of solubility and K_{ow}. They noted that compounds within a class are toxic at a relatively constant fraction of their water solubility. Alkanes, for example, are acutely toxic to *D. magna* at 25 to 57% of their solubility, cycloalkanes at 7 to 11%, monoaromatics at 1 to 14%, and polyaromatics at 5 to 64% (Table 4-1). Bobra *et al.* (1983a) suggested that compounds within a class cause toxic effects at similar internal concentrations, and that differences in LC_{50} values are due to differences in biological uptake. Because compounds with higher K_{ow} are taken up more readily, lower aqueous concentrations can cause internal concentrations to reach toxic levels.

The toxicity of aromatics often tends to increase with oxygen, nitrogen, or sulfur substitution (Giddings, 1979; Bringmann and Kühn, 1980; Heldal *et al.*, 1984). Heldal *et al.* (1984) measured the toxicity of eleven aromatic photooxidation products to the green alga *Dunaliella bioaculata* (Table 4-5). Quinones and hydroperoxides were the most toxic photoproducts tested, phenols and and carboxylic acids the least. Similar findings were reported by Larson *et al.* (1977) for baker's yeast, and by Giddings (1979) for the alga, *Selenastrum capricornutum.*

The sensitivity of aquatic species to petroleum constituents varies widely and inconsistently. The EPA's AQUIRE database (AQUIRE, 1996) contains acute toxicity data for a broad range of species. Table 4-6 summarizes acute toxicity data for benzene, toluene, xylene, naphthalene, and anthracene for freshwater fish, invertebrates, and algae. Only conventional acute toxicity endpoints (LC_{50}s) were included in the summary. When several results were available for a given species, the geometric mean of the reported LC_{50} values was calculated.
Though few clear trends emerged from this exercise, some broad generalizations can be made. Most of the LC_{50} values for monoaromatics were between 10 and 100 mg/L. LC_{50}s for naphthalene were generally between 1 and 10 mg/L. Three of the four values for anthracene were less than 1 mg/L. Müller (1987) attempted to generalize about hydrocarbon toxicity and species sensitivities (Figure 4-1). She noted that aromatic compounds with four or more rings are generally not acutely toxic at their solubility limits in water, an extension of the trend observed by Bobra *et al.* (1983a).

Rainbow trout, a common toxicity test organism, were consistently among the most sensitive species to petroleum hydrocarbons, and algae were often among the most tolerant. However, such generalizations cannot be given too much weight because the variability of LC_{50} values is due to many factors other than differences between species. These factors include the age and source of the test organisms, temperature, water quality (such as pH and hardness), exposure duration, exposure regime (static vs. flow-through), closed versus open test vessels, measured versus nominal chemical concentrations, and other aspects of laboratory technique.

Table 4-5. Acute toxicity of photooxidation products to *Dunaliella bioculata* (green algae).

Compound	72-hr EC_{50} (mg/L) [a]	Structure
1-naphthoic acid	55.6	
1-naphthol	14	
1,2-naphthoquinone	1.0	
Tetralinhydroperoxide	0.71	
1,4-naphthoquinone	0.011	
9-hydroxyfluorene	27	
Fluorene	15.5	
9-fluorenone	5.7	
9-fluorenehydroperoxide	0.50	
9,10-epoxy-9,10-dihydrophenanthrene	0.55	
9,10-phenanthroquinone	0.38	

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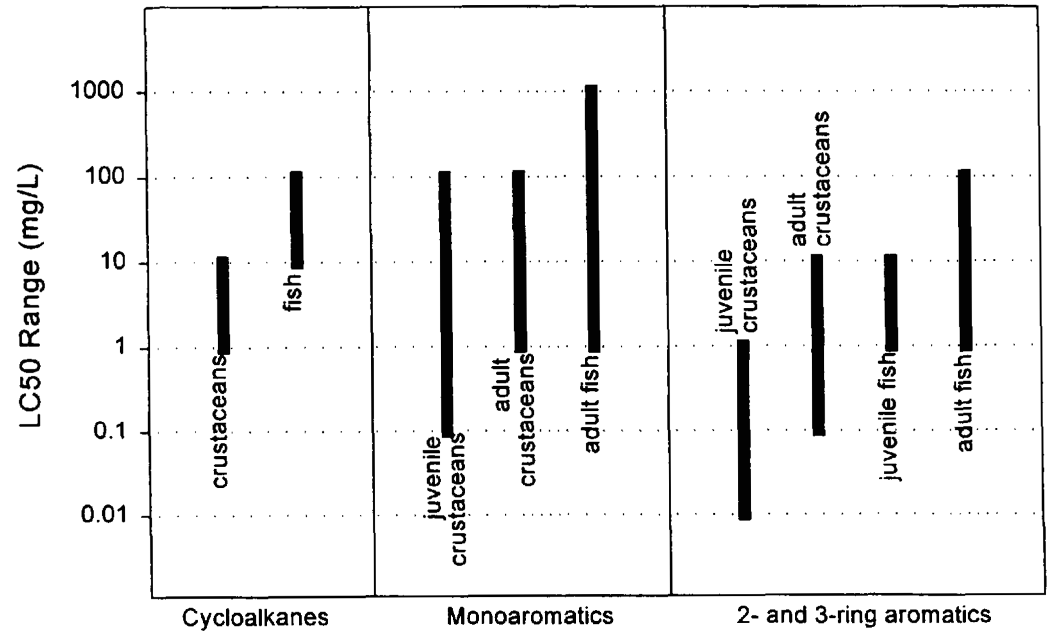
[a] EC_{50} is the concentration required to produce an effect in 50% of a test population.
Source: From Heldal *et al.*, 1984.

Table 4-6. Acute toxicity of aromatic hydrocarbons to freshwater organisms.

			LC_{50} values (mg/L)		
Species	Benzene	Toluene	Xylene	Naphthalene	Anthracene
Fish (96-hr LC_{50})					
Bluegill sunfish		346	18		0.0072
Carp			780		
Channel catfish		240			
Clarias catfish		26			
Coho salmon				2.6	
Fathead minnow		36	25	4.9	25
Goldfish		23	24		
Guppy		41			
Largemouth bass				0.59	
Medaka		54			
Mosquitofish		1200		150	
Rainbow trout	7.4	8.9	8.2	3.4	
Zebrafish		25	20		
Invertebrates (48-hr LC_{50})					
Aedes aegypti (mosquito)	59	22	14		0.001
Brachionus calyciflorus (rotifer)		110	250		
Chironomus attenuatus (insect)				15	
Chironomus tentans (insect)				2.8	
Daphnia magna (zooplankton)	30	41		6.3	0.43
Daphnia pulex (zooplankton)				9.2	
Diaptomus forbesi (zooplankton)		450	100	68	
Gammarus lacustris (amphipod)			0.35		
Gammarus minus (amphipod)				3.9	
Physa gyrina (snail)				5.0	
Somatochlora cingulata (insect)				1.0	
Algae (EC_{50}, various exposure times)					
Chlamydomonas angulosa		130		9.6	
Chlorella vulgaris		230		25	
Microcystis aeruginosa				0.85	
Nitzschia palea				2.8	
Scenedesmus subspicatus		130			
Selenastrum capricornutum	70	25	72	7.5	

Source: Data from AQUIRE (1996). Where more than one toxicity value was reported for a species, the geometric mean is given.

Figure 4-1. Ranges of acute toxicity of petroleum hydrocarbons to freshwater organisms.



Source: Adapted from Müller, 1987.

COMPARATIVE TOXICITY OF OIL WATER SOLUBLE FRACTIONS AND DISPERSIONS

Dissolved vs. Dispersed Oil

The toxicity of an oil to aquatic organisms is due mainly to its water soluble components. This is largely a matter of exposure: Undissolved oil components tend to remain in the surface slick, while organisms living in the water beneath the slick are exposed only to the components that have dissolved into the water. However, even when oil droplets are dispersed in the water, the insoluble components they contain have relatively little toxicological impact. Because of their hydrophobicity and lipophilicity (quantified by K_{ow}), petroleum hydrocarbons are readily taken up by organisms from water but not from oil. However, dispersed oil droplets my have physical effects due to coating of gill membranes or appendages.

For example, Woodward *et al.* (1981) exposed cutthroat trout to oil-in-water dispersions (OWDs) of Wyoming crude. The oil (and the OWD) contained 80% C_7 - C_{30} alkanes, 10% substituted naphthalenes, and 10% other aromatics. After 90 days, hydrocarbon concentrations were measured in the trout, and an apparent bioconcentration factor (BCF, the tissue concentration divided by the OWD concentration) was calculated for each fraction. The average BCF for alkanes was 8. BCFs for alkyl-substituted mono- and diaromatics ranged from 148 to 447; for triaromatics, BCFs ranged from 18 to 163. These apparent BCFs were inconsistent with the relative K_{ow} values of the three fractions. Because C_7 - C_{30} alkanes and triaromatics have higher K_{ow} values than mono- and diaromatics (see Table 3-7), they would be expected to have higher tissue cocentrations than mono- and diaromatics in fish. The apparent discrepancy has a simple explanation: most of the aliphatics and triaromatics in the OWD were present in the oil droplets, from which they were relatively unavailable for uptake by fish. If the BCF calculations were based only on the compounds in solution, the BCFs probably would have been more consistent with the K_{ow} values.

Trucco *et al.* (1983) measured the uptake of aromatic hydrocarbons by *Daphnia pulex* (zooplankton) from water and from food (algae). The results are shown in Table 4-7. Bioconcentration factors for dissolved aromatics followed the expected trend, consistent with K_{ow} values. However, BCF values from food declined from naphthalene through benzo(a)pyrene. The explanation may be similar to that for uptake from OWD (Woodward *et al.*, 1981). That is, the polyaromatic hydrocarbons remained bound to the food, even in the digestive tract of the daphnids, rather than being available for uptake. As in the OWD example, uptake was greatest for the diaromatic hydrocarbons, which are lipophilic enough to partition into tissues but soluble enough to be bioavailable.

Not surprisingly, therefore, most work on the toxicity of oils has focused on water soluble fractions (WSFs). As expected, oils containing higher proportions of relatively soluble constituents produce WSFs that are more toxic to aquatic organisms. Before discussing these results, however, it will be useful to review the techniques used for preparing and characterizing exposure solutions for oil toxicity tests.

Table 4-7. Bioaccumulation of aromatic hydrocarbons by *Daphnia pulex* (zooplankton).

Compound	BCF (water)	BCF (food)	BCF (combined)
Benzene	225	203	153
Naphthalene	677	10844	2337
Phenanthrene	1165	1032	1424
benzo(a)anthracene	1106	458	803
benzo(a)pyrene	2720	745	1259

Source: From Trucco *et al.*, 1983.

Oil Toxicity Testing Methods

The traditional method for generating a WSF for toxicity testing is to float a measured volume of oil on a measured volume of water (typically 1 part oil to 10 parts water), stir gently for 24 to 48 hours, allow the mixture to settle so dispersed oil droplets can rise to the surface, and carefully remove the underlying water. Often the WSF is filtered or centrifuged before use to remove any remaining oil droplets. (Girling *et al.*, 1992, do not recommend filtration because of the possibility of dissolved components adsorbing to the filter.) Some oils are prone to produce emulsions that are difficult to separate; the resulting mixtures are termed "water accommodated fractions" (WAFs) to distinguish them from true WSFs (Girling, 1989). CONCAWE (1993) prefers the term WAF for any test solution that has not been centrifuged or filtered. Today, the terms are used almost interchangeably.

An alternative to WSF or WAF preparation is to mix the oil-water mixture energetically and create an oil-water dispersion (OWD) for toxicity testing. Various approaches may be used to maintain homogeneity of the OWD. In a static test (no replacement of exposure solution), mixing may be provided continuously throughout the test to maintain the dispersion; small test organisms need to be isolated from the mixing apparatus to prevent physical damage. In a flowthrough test (continuous replacement of exposure solution), an OWD may be prepared continuously and distributed immediately to the exposure vessels (e.g., Woodward *et al.*, 1981; Hedtke and Puglisi, 1982). A third method for exposing test organisms to oils, not often used, is to create artificial slicks directly in the test chamber (e.g., Hedtke and Puglisi, 1982; Vandermeulen, 1990).

Most toxicity tests involve a series of exposure concentrations so the LC_{50} or the NOEC may be determined. Concentration series of WSFs, WAFs, and OWDs can be prepared in two ways: by diluting the highest concentration with uncontaminated water, or by using a different oil-to-water ratio ("loading rate") to prepare each concentration. Because various oil constituents partition differently between the oil and the water, the two methods may produce WSFs with different compositions. If a dilution series is used, it is assumed that the proportions of dissolved constituents are constant in all solutions in the series. This assumption may not be correct for insoluble materials, like petroleum hydrocarbons. If different loading rates are used, the proportions will vary. Concentrations of less soluble constituents may be nearly the same regardless of the loading rate, while concentrations of more soluble constituents will be lower at lower loading rates. As a result, the proportion of less soluble constituents increases at lower loading rates.

CONCAWE (1993), followed recently by ASTM (1996), recommends the second approach and specifies that exposure should be expressed in terms of loading rate. Many investigators, however, continue to use the first approach (which is more consistent with standard toxicological methods with water soluble materials), and express exposure in terms of percent of full-strength WSF. Neither approach is directly applicable to prediction of effects from an actual spill because neither the loading rate nor the percent WSF is meaningful except under controlled hydrological conditions in a laboratory. Either approach can be useful for comparing the toxicity of different oils, provided the mixing conditions are standardized. The loading rate approach may lend itself better to comparisons between laboratories: A 1 mg/L loading rate of a given oil should always produce the same WSF, whereas two 0.1% WSFs prepared by dilution may be different depending on the oil-to-water ratio used to produce the full-strength WSFs. However, WSF composition depends on many procedural details, besides the loading rate, including the absolute oil and water volumes, shape and size of the mixing vessel, mixing technique, mixing time, ambient temperature, headspace, and separation technique.

The clearest way around these difficulties is to measure concentrations of oil constituents in the exposure solution, and express toxicity in terms of those concentrations. Of course, this method presents a considerable analytical challenge, and interpretation of the results depends on an understanding of the individual and additive effects of the constituents.

Relative Toxicity of Oils

Of the many reported studies of WSF toxicity to freshwater organisms, that of Lockhart *et al.* (1987) is particularly revealing of the relationship between chemical composition and toxicity. These investigators measured the toxicity of WSFs of Norman Wells crude oil, No. 1 fuel oil (kerosene), diesel oil, and unleaded gasoline to rainbow trout. They analyzed the WSFs for hydrocarbons with boiling ranges <115°C (by headspace GC) and 115 to 270°C (by solvent extraction). The <115°C fraction consisted of C_1 - C_7 alkanes, benzene, and toluene. The 115 to 270°C fraction included ethyl benzene, xylenes, cumene and other C_3-substituted benzenes, methylnaphthalenes, and dimethylnaphthalenes.

The chemical composition and toxicity of the WSFs are presented in Table 4-8. The WSFs of Norman Wells crude and unleaded gasoline were rich in light hydrocarbons, while the WSFs of No. 1 fuel oil and diesel oil contained very little of this fraction. The gasoline WSF contained 115-270°C hydrocarbons at concentrations two to three times higher than the WSFs of the other oils. In terms of percent WSF, unleaded gasoline was the most toxic, reflecting its high concentrations of both dissolved hydrocarbon fractions. Crude oil and No. 1 fuel oil WSFs were intermediate, and diesel oil WSF was the least toxic.

In terms of total measured hydrocarbons, a different picture of relative WSF toxicity emerged. LC_{50} values ranged from 1.6 mg/L to 10.4 mg/L, consistent with the LC_{50} range for benzene, toluene, xylene, and naphthalene for rainbow trout (Table 4-6). The toxicity of the WSFs was roughly proportional to their percentage of 115-270°C aromatics: the WSF of No. 1 fuel oil (91% 115-270°C) was the most toxic, while the WSF of crude oil (15% 115-270°C) was the least toxic. If the contribution of the lighter fraction to WSF toxicity is ignored, the LC_{50} values can be calculated in terms of mg/L of the 115-270°C fraction. These LC_{50}s were very consistent, varying only from 1.01 to 2.06 mg/L for the four WSFs.

The similarity of WSF LC_{50}s in terms of 115-270°C aromatics (Lockhart *et al.*, 1987) implies that these compounds (alkylated benzenes and naphthalenes) were primarily responsible for overall WSF toxicity. Most other investigators have reached the same conclusion: the toxicity of oils to aquatic organisms is related to their concentrations of polyalkylated mono- and diaromatic constituents.

Bobra *et al.* (1983b) measured the toxicity of four crude oils, a natural gas condensate, and a synthetic oil mixture to *Daphnia magna* (zooplankton). The four crude oils were similar in their WSF composition and their acute toxicity to *D. magna* (Table 4-9). The results for these WSFs were consistent with those of Lockhart *et al.* (1987) for Norman Wells crude: LC_{50} values ranged from 26 to 32% WSF and from 7.4 to 9.4 mg/L total hydrocarbons. The WSFs of natural gas condensate and the synthetic oil mixture contained higher BTEX concentrations than the crudes, and were more toxic in terms of percent WSF (12% and 7%, respectively), but not in terms of total hydrocarbons (9 and 13.5 mg/L, respectively). LC_{50}s calculated in terms of polyalkylated benzenes and "residue" (non-BTEX constituents) ranged from 2.0 to 3.5 mg/L (not shown in Table 4-9).

Table 4-8. Acute toxicity of WSFs of four oils to rainbow trout.

WSF	Concentration (mg/L)		48-hr LC_{50}			
	<115°C	115-270°C	% WSF	Total (mg/L)	<115°C (mg/L)	115-270°C (mg/L)
Norman Wells crude	41.2	7.6	26	10.4	8.85	1.55
No. 1 fuel oil (kerosene)	0.55	5.4	26	1.63	0.15	1.48
Diesel fuel	1.2	6.7	34	2.43	0.37	2.06
Unleaded gasoline	63.0	15.2	8	6.80	5.79	1.01

Source: From Lockhart *et al.*, 1987.

Table 4-9. Composition of crude oil WSFs and toxicity to *Daphnia magna* (zooplankton).

		Concentration in water (mg/L)					LC_{50}	
Oil	% evaporated	Benzene	Toluene	C_2 benzenes and cumene	Residue	Total	mg/L	% WSF
Norman Wells	0	12.0	7.6	2.3	10.3	32.3	9.0	28
	20.4	1.8	2.3	1.8	1.4	7.3	4.4	60
Prudhoe Bay	0	11.1	8.3	3.7	6.2	29.3	9.4	32
	24.4	0.040	0.051	0.002	0.009	0.102	>0.1[a]	>100
Lago Medio	0	7.12	6.58	3.51	8.3	25.5	7.7	30
	22.3	0.013	0.012	0.006	0.58	0.61	>0.6[a]	>100
Murban	0	7.88	7.77	4.53	8.44	28.62	7.4	26
Natural Gas Condensate	0	22.08	32.34	13.36	6.97	74.65	9	12
	42	0.002	0.024	2.76	5.23	8.02	2	25
Synthetic Oil Mixture[b]	0	114	61.1	19.4	8.9	203.4	13.5	7

Source: From Bobra *et al.*, 1983b.

[a] 50% mortality not achieved in full-strength WSF

[b] Benzene (10%), methyl cyclohexane (10%), toluene (10%), octane (5%), p-xylene (10%), 1,2,4-trimethylbenzene (5%), decane (5%), naphthalene (5%), dodecane (5%), tetradecane (30%), phenanthrene (5%)

Bobra *et al.* (1983b) determined how simulated weathering of the oils (evaporation in a wind tunnel) affected WSF composition and toxicity. Evaporation of 20 to 40% of the oil volume from Prudhoe Bay and Lago Medio crudes resulted in WSFs with almost no measurable hydrocarbons and no toxicity to *D. magna* (Table 4-9). This result was confirmed in field investigations associated with the *Exxon Valdez* spill (Neff and Stubblefield, 1995). The WSF of weathered Norman Wells crude retained about 15% of the benzene, 30% of the toluene, and nearly 80% of the ethyl benzene, xylenes, and cumene present in the WSF of the unweathered oil. Its toxicity measured as percent WSF was reduced by about one-half (compared with WSF of the unweathered oil), but its toxicity measured as total hydrocarbons doubled, reflecting the greater proportion of the more toxic components. Weathering had a similar effect on the natural gas condensate, except that the non-BTEX components (identity unknown) were preferentially retained; again, toxicity decreased in terms of percent WSF but increased in terms of total hydrocarbon concentration. The authors pointed out that there is "no simple answer to the question of whether or not weathering reduces the toxicity of oil; it depends on the definition of toxicity."

These results suggested that the toxicity of a WSF (in terms of both percent WSF and mg/L) should be predictable from its composition, especially its aromatic content. Bobra *et al.* (1983b) explored this possibility with a toxicity additivity model. The contribution of each measured WSF component to WSF toxicity can be expressed by the ratio of its concentration in the WSF to its individual LC_{50}. The toxicity of the mixture (the WSF) can then be estimated by summing the contributions from each component. Using this approach, Bobra *et al.* (1983b) were able to predict the toxicity of each WSF based on its composition. The predicted WSF LC_{50}s agreed closely with the measured LC_{50}s ($r^2 = 0.96$). The applicability of this method would be limited by knowledge of the toxicity of individual oil constituents and by the assumption that the toxicities are additive. Nevertheless, the results of Bobra *et al.* (1983b) imply that estimation of oil toxicity from oil composition is a promising approach.

The studies of Lockhart *et al.* (1987) and Bobra *et al.* (1983b) illustrate two important aspects of comparative oil toxicity: First, the toxicity of an oil is generally predictable from its composition, particularly its content of alkylated mono- and diaromatics; second, the acute toxicity of WSFs (expressed in mg/L) is similar to that of individual mono- and diaromatics. Other studies extending these observations to a wider range of oils and organisms are reviewed in the following paragraphs.

Rogerson *et al.* (1982) measured the effects of ten crude oils on the rotifer, *Asplanchna sieboldi*. The organisms were exposed to whole oils, and toxicity was expressed in terms of loading rate (µL oil per mL of medium). Effects were measured as survival and reproduction over an 18-hour exposure, relative to unoiled controls. The toxicity was highest for lighter, more volatile oils (including Norman Wells and Prudhoe Bay crudes). Heavier, more viscous oils (including Lago Medio crude) were less toxic. For many of the oils, effects were more severe when the cultures were shaken, presumably because shaking enhanced dissolution.

Geiger and Buikema (1982) reported that the WSF of No. 2 fuel oil was less toxic to *Daphnia pulex* (in terms of percent WSF) than the WSF of creosote. The WSFs in this study were aerated, however, which probably removed most of the lighter components of the No. 2 WSF (as demonstrated by Soto *et al.*, 1975a; Bobra *et al.*, 1983b; and Lockhart *et al.*, 1987).

Several investigators have measured effects of oils and WSFs on freshwater algae. Soto *et al.* (1975a) tested WSFs of two crude oils (BP Mixed Blend Sour and Bow River crudes) using the motile green alga *Chlamydomonas angulosa*. Both WSFs temporarily immobilized the algae, but they soon regained motility. The WSF of BP Mixed Sour Blend caused a lag in algal growth. The WSF of Bow River crude completely inhibited growth, but growth resumed when the culture flasks were opened. When the WSFs were left open to the air for 7 days before inoculation, they had no effect on the algae, implying that the toxicity of the WSFs was due to volatile components.

Gaur and Kumar (1981) exposed four algal species to filter disks treated with three crude oils and "furnace oil." Furnace oil was the most toxic to all four species. The two least sensitive species (*Chlorella vulgaris* and *Oocystis* sp.) were collected from a river polluted by refinery and chemical effluents, possibly indicating adaptation or selection for hydrocarbon tolerance.

Giddings *et al.* (1980) measured the effects of petroleum and coal-oil WSFs on *Daphnia magna* and two species of freshwater algae. In terms of percent WSF, No. 6 residual oil was least toxic (no effect at full strength), No. 2 fuel oil was more toxic, and coal oil was most toxic. The coal oil WSF contained 50 times as much dissolved organic carbon as the WSF of petroleum-derived No. 2 fuel oil. More than half of the coal oil WSF consisted of phenols. Among the petroleum WSFs, toxicity was lowest (in terms of percent WSF) for No. 6 and JP-5 products; No. 2 fuel oil and marine diesel fuel were more toxic. Millemann *et al.* (1984b) confirmed the relative toxicity of No. 2 fuel oil, shale oil, and coal oil WSFs to two species of freshwater snails.

Tagatz (1961) measured the toxicity of gasoline, No. 2 fuel oil, and Bunker C to American shad (*Alosa sapidissima*). In terms of loading rates, gasoline was the most toxic, and Bunker C the least, consistent with the presumed solubilities of these mixtures in water. The oils were applied as surface slicks, which were found to interfere with oxygen diffusion from the air into the water. Oxygen depletion under the gasoline slick increased the apparent sensitivity of the fish to the oil.

Moles *et al.* (1979) tested six species of Alaskan salmonids (Dolly Varden, chinook salmon, coho salmon, sockeye salmon, arctic grayling, and arctic char), as well as slimy sculpins and threespine stickleback, with the WSF of Prudhoe Bay crude oil. The LC_{50} values (total hydrocarbons) for the six salmonids, exposed as juveniles, ranged from 2.7 to 4.4 mg/L. Slimy sculpins were more tolerant (LC_{50} 6.44 mg/L), and threespine stickleback were unaffected by full-strength WSF (10.45 mg/L). In tests with benzene alone, Moles *et al.* (1979) determined that earlier life stages of pink and coho salmon were much less sensitive than juveniles. LC_{50} values for embryos were 30 to 40 times higher than LC_{50} values for emerging fish (90-day old fish that had completed their early stages of development and were emerging from the gravel). Sensitivity increased steadily between the embryo and emergence stages. The reasons for the tolerance of embryos and larvae were not confirmed, but it was suggested that eggs and larvae can partition aromatic hydrocarbons into the yolk, so the developing fish is exposed to small quantities at a slow rate as the yolk is consumed.

Hedtke and Puglisi (1982) measured the toxicity of WSFs, OWDs, and floating oils to fish and amphibians. With OWDs, they determined that toxicity to fathead minnows was highest for mixed blend sweet crude, less for No. 2 fuel oil, and least for No. 1 fuel oil (kerosene). With larvae of the frog *Rana sylvatica*, OWD toxicity was highest for No. 2 fuel oil, less for crude oil, and least for No. 1 fuel oil (kerosene). Used crankcase oil was more toxic to both species than No. 2 fuel oil in terms of percent WSF or floating oil loading rate.

Aquatic toxicity data are most frequently used as an indicator or predictor of environmental impact. For poorly soluble materials like petroleum, the test methods developed for water soluble materials have limitations. Our current understanding is that an oil's toxicity is generally related to the concentration of polyalkylated mono- and diaromatic constituents. *In–situ* toxicity will vary with the composition of an individual oil in conjunction with composition changes due to weathering. Improvements in data quality and results interpretation will increase with use of appropriate test methods. More information is desirable to clarify the relationship of whole oils (what is spilled and weathering), soluble fractions (what is toxic), and WSFs (what is created for testing purposes). Further, better documentation is needed on actual exposure concentrations (doses).

EFFECTS OF OILS ON FRESHWATER ORGANISMS

The preceding section reviewed data on the relative toxicities of petroleum constituents and whole oils, and on the relative sensitivity of freshwater species. A more complete description of the toxicological effects of oils and their constituents on various groups of organisms follows.

Bacteria and Other Microbes

Aquatic bacteria, fungi, protozoans and other groups of microorganisms are typically discussed as a unit with respect to oil spill effects. Bacteria have received the greatest attention, most likely as a result of the ecologically important role they play in the biodegradation of spilled petroleum products. As with other types of organisms, studies of effects of oil spills on microorganisms predominately concern the marine environment. However, sufficient information is available in the literature regarding the effects of petroleum products on freshwater microorganism communities to formulate some consensus (Shales *et al.*, 1989). Prior reviews on the subject include Shales *et al.* (1989) and Atlas (1985).

Based on the findings of various investigations into the effects of hydrocarbons on freshwater microbial populations, there appears to be no generalized, widescale toxic effect (Shales *et al.*, 1989). Many studies, as will be discussed, have reported a stimulatory effect of oil on total bacteria densities, or at least on the hydrocarbon-utilizing groups of bacteria. In fact, the total number of hydrocarbon-utilizing bacteria present in a water body, or the relative proportion of such bacteria compared to the total number of bacteria present, has been regarded as a potential forensic index of the extent of past and present hydrocarbon impacts (Atlas, 1981).

Hydrocarbon Toxicity. Few studies have directly measured hydrocarbon toxicity to microorganisms under controlled conditions[1], and little, if anything, is known regarding toxicological mechanisms. However, several observational investigations are available detailing bacterial population responses to hydrocarbon additions.

Most studies report some form of stimulatory effect of hydrocarbons on bacterial populations. Lock *et al.* (1981a) dipped limestone bricks into synthetic crude oil and then tracked subsequent bacterial colonization of the brick surfaces in a river system. Up to nine times more bacteria were observed on oiled bricks than un-oiled ones. In a companion study, the same authors applied oil to bricks already bearing established bacterial populations and monitored subsequent responses. Some minor increases in total numbers of bacteria present were seen among oiled bricks as compared to un-oiled ones (Lock *et al.*, 1981b). The authors presumed that at least some portion of the increase in total numbers of bacteria was attributable to the proliferation of oil-degrading bacteria, although specific identifications were not conducted.

Lock's *et al.* (1981a, b) results confirm those of other studies reporting lack of toxicity and increased numbers of total bacteria following the addition of crude oil and petroleum products to freshwater systems. Hutchinson *et al.* (1976) observed increased numbers of bacteria in an arctic lake following exposure to crude oil. Shindler *et al.* (1975) reported stimulation of bacterial populations in freshwater artificial ponds following crude oil addition. They also detected a relationship between increases in total bacteria numbers and the concentration of crude oil present in the ponds. Horowitz and Atlas (1977) found increased numbers of microbes in water and sediment samples from an arctic lake contaminated with gasoline. Werner *et al.* (1984, 1985) reported a rapid stimulatory response to, and no toxic effect of, crude oil among decomposer bacteria groups in freshwater mesocosms simulating Rocky Mountain region lakes. The authors observed no lag time associated with the acclimation and enhancement of decomposers to the spilled oil.

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[1] It should be noted that a laboratory bioassay methodology has been developed using luminescent bacteria. Microtox® is a toxicity testing system that exposes bacteria to environmental samples and monitors their response. Standard toxicological endpoints (EC_{50}) can be determined, and numerous compounds have been tested (Eisman *et al.*, 1991). However, the ecological significance of Microtox® results is unclear; therefore, they will not be reviewed here.

Dutka and Kwan (1984) reported that the addition of oil and oil dispersants has no discernable negative effects. Some stimulatory effects on microbial biomass in man-made freshwater ponds were observed, but enhancement was short-term. Oil and oil plus dispersant microbiota did not display mutagenic activity or toxic effects. One of the explanations offered by the authors for this observation was that the test systems were not sufficiently sensitive to detect mutagenic and toxic effects. Alternatively, toxic activities could be due to physical effects (i.e., blocking of respiratory apparatus) and, thus, microbes are unaffected. The authors concluded that their data confirmed that the release of oil into aquatic environments was not an especially stressful event to the microbial portion of the biota.

Increased numbers of bacteria following petroleum additions have not been reported without exception. Jordan *et al.* (1978) noted increased numbers of bacteria following an experimental crude oil spill into an oligotrophic arctic lake; however, increases were significant only during a single summer month (spill in July 1976, significant increase only in June 1977). The authors found no effect of oil exposure on numbers of bacteria in the lake sediments, and detected no effect on glucose turnover rates in the lake. Glucose turnover has been used as an indicator of bacterial activity, and has been shown to be variably affected by petroleum exposure in other studies (inhibited among marine bacteria by >300 parts per billion [ppb] No. 2 fuel oil or crude oil, as reported by Hodson *et al.*[1977]; inhibited and stimulated among marine sediment bacteria by exposure to No. 2 fuel oil, as reported in unpublished studies conducted by Jordan). Bergstein and Vestal (1978) found that addition of Prudhoe Bay crude oil to an arctic tundra pond did not significantly increase numbers of oil degrading or total heterotrophic bacteria over a 28-day observation period.

Microorganism Community Alterations. Although most studies investigating the responses of microorganisms to petroleum additions have documented increases in total microbial biomass, only a limited number have characterized community changes following the additions. Those studies noting changes have reported significant alterations in the types of bacteria present in a water body before and after hydrocarbon pollution. Although total numbers of bacteria may increase or remain constant, diverse microbial communities tend to be replaced by near monocultures of oil-resistant or oil-utilizing species.

Atlas (1985) identified certain bacteria as hydrocarbon-utilizing and noted that, in unpolluted systems, these organisms comprised less than 0.1% of the microbial community. In contrast, in oil-polluted systems, the number approaches 100%. Horowitz and Atlas (1977 and unpublished data reported in Atlas [1985]) observed a dramatic decline in microbial species diversity and a rapid shift to hydrocarbon-utilizing microorganisms following a gasoline spill into an arctic coastal lake. Bacterial biomass remained essentially constant; however, in the heavily contaminated region of the lake, *Pseudomonas* sp. replaced all other species of bacteria. The species shift was attributed to both the presence of toxic components in the refined petroleum product and the ability of surviving *Pseudomonas* to tolerate and metabolize the hydrocarbons in the spilled fuel.

Similar results were reported for temperate freshwater systems by Atlas and Bartha (1973) and Walker and Colwell (1976b). Gillespie and Vaccaro (1981) suggested that the stimulation of carbon-utilizing bacteria following an oil spill was attributable to the presence of a readily available carbon source. The researchers indicated that the stimulation was not a compensatory response to reduced competition and predation from oil-sensitive species.

Reports of bacterial stimulation following oil spills, thus, may not comport with a complete lack of toxicity to bacterial species. Community responses and stimulation of tolerant species may mask and compensate for adverse effects on some organisms. Also, because hydrocarbon-utilizing bacteria normally comprise only a small portion of the total microbial community, enhancement of hydrocarbon-utilizing species may not be noticeable as an increase in the total microbial population following an oil spill (Jordan *et al.*, 1978).

<u>Ecological Effects of Oil Additions</u>. Several studies have evaluated the potential effect of oil spills on bacteria as they relate to oxygen demand, nutrient cycling, and litter decomposition in freshwater systems. Spilled oil can provide a carbon source that bacteria use as an alternative to naturally occurring plant litter. As a result, decomposition may be inhibited and normal

patterns of nutrient cycling in the system adversely affected. Surface water concentrations of nitrogen and phosphorous have been found to control strongly the rate of oil-derived hydrocarbon utilization by freshwater bacteria. According to Atlas (1985), environmental factors related to the nutritional status of a water body will have a major effect on the extent of change in relative numbers of bacteria and bacterial activity before and after hydrocarbon addition.

Oil spills into freshwater systems can significantly alter oxygen exchange dynamics as a result of their effects on bacteria populations. Biodegradation of oil primarily occurs by aerobic bacteria and, thus, is an oxygen-demanding process. Intense biodegradation may lead to the occurrence of anoxic conditions, especially in confined water bodies (Werner *et al.*, 1985). Consequent impacts on fish and other aquatic animals may result. At the same time, oxygen exchange between the water surface and atmosphere may be inhibited by the presence of an oil slick, further limiting dissolved oxygen concentrations. Toxicity to photosynthetic algae will cause further reductions in dissolved oxygen concentrations. Enhanced bacterial activity, coupled with these other oxygen-limiting processes, therefore, may result in pronounced adverse effects on dissolved oxygen-dependant freshwater biota.

Spilled oil may dramatically alter bacteria-related processes that control freshwater nutrient concentrations, specifically of nitrogen and phosphorous. Petroleum products provide bacteria and other detritivores with a ready source of highly reduced carbon, similar to naturally occurring organic material (such as dead plant matter). Following petroleum additions to freshwater systems, bacteria have been shown to switch from plant litter to spilled oil as a primary carbon source. This switch may result in the reduction of plant litter decomposition rates (Werner *et al.*, 1984; McKinley *et al.*, 1982).

Unlike other naturally occurring organic material, many petroleum products contain little or no accompanying phosphorous or nitrogen (Werner *et al.*, 1984). These nutrients are utilized by the bacteria consuming the oil and are essential to the growth and maintenance of algal populations. When bacteria shift to spilled oil as their carbon source, significant reductions in surface water nitrogen and phosphorous concentrations may result. Less of these nutrients are released from the bottom litter, and more are immobilized from the water column by decomposers oxidizing the spilled oil.

Werner *et al.* (1984) suggest that one of the greatest impacts of oil pollution on freshwater systems may be the effect on the rate and extent of nutrient release from decomposing plant litter. Werner *et al.* (1985) further suggest that oil-stimulated declines in surface water concentrations of essential nutrients, as opposed to toxicity, represent the primary factor causing long-term reductions in plant and algal biomass following oil spills. In an unpolluted water body, nutrients released from plant matter decomposition are needed to maintain productivity. Oil pollution immobilizes the nutrients, causing a nutrient imbalance and reduced productivity in the water body (Werner *et al.*, 1984). Reduced nutrient concentrations may also inhibit further bacterial oil biodegradation (Atlas *et al.*, 1976; Horowitz and Atlas,1977; Werner *et al.*, 1984).

Fertilization of oil-impacted freshwater systems may offset the effects of decreased nutrient mobilization and may stimulate the biodegradation of spilled oil (Atlas *et al.*, 1976). Agricultural wash-off into some systems may also be sufficient to compensate for spill-derived changes in nutrient cycling (Shindler *et al.*, 1975). Highly eutrophic lakes may contain sufficient nutrient concentrations such that nutrient limitations do not occur. However, these systems will be especially susceptible to dissolved oxygen crashes and the resulting impacts on freshwater animals.

Algae

In general, petroleum hydrocarbons do not appear to be as directly toxic to freshwater algae when compared to other organisms such as fish and invertebrates (Tables 4-3 and 4-6). Instead of decimating algal populations, oil spills often stimulate algal production after an initial depression in primary production. As with other types of organic pollution, it appears that this stimulation is a result of an influx of limiting nutrients. It has been postulated that the oil itself does little to stimulate algal growth, as oil is mainly carbon and hydrogen. Instead, it has been observed that nitrogen-fixing cyanobacteria populations increase as well and provide limiting nutrients. This population increase may account for the increase in primary production. It also may serve to offset the heightened nutrient demands created by stimulation of hydrocarbon utilizing heterotrophic bacteria, as was previously discussed.

While petroleum hydrocarbons in freshwater systems can have a stimulatory effect on algal populations, there is typically an initial lag or inhibitory phase following exposure. This lag period may be due to organismal responses such as decreased growth (Heldal *et al.*, 1984; Soto *et al.*, 1975a) or to more localized cellular effects such as membrane disruption (Herman *et al.*, 1991; Hutchinson *et al.*, 1981) or photosynthetic inhibition (Giddings, 1979; Soto *et al.*, 1975b) caused by the more toxic compounds.

A recovery phase occurs approximately 2 to 4 days following initial exposure. This phase has been linked to the loss of the more toxic and volatile compounds, although it is probably more dependent on the type of species and hydrocarbons present. While there are reports that a stimulatory phase can follow the recovery phase, population increase is likely a result of both increased nutrient supply (Shales *et al.*, 1989) and decreased herbivore populations (Miller *et al.* 1978).

Primary Effects. While the toxic effects of oil components on algae do not appear to be long-lasting, it has been documented that there are several methods by which petroleum hydrocarbons impact algae. Oils and oil products have been shown to decrease algal growth and mobility (Gaur and Kumar, 1981; Heldal *et al.*, 1984; Kauss *et al.*, 1973; Soto *et al.*, 1975a). Growth rates of several different algal species have been reported to be reduced initially after oil exposure but then to recover to pre-exposure levels 2 to 4 days afterward. Soto *et al.* (1975a) demonstrated that this initial decrease in growth was due to the more toxic volatile hydrocarbons (i.e., BTEX) by comparing growth rates in open and closed systems. Thus, after the toxic components have volatilized, growth rates return to normal. However, it has also been suggested that different oil products may impact the algal cell differently. Heldal *et al.* (1984) demonstrated that several photodecomposed hydrocarbons depressed overall growth rates of the green alga, *Dunaliella bioculata,* although growth remained exponential. This reduction in growth rate was also reported for microalgae exposed to No. 2 fuel oil and Phenalen-1 (Pulich *et al.*, 1974; Winters *et al.*, 1977).

Although several studies have measured only gross endpoints such as biomass or mobility, other studies have attempted to elucidate the toxic mechanism by monitoring endpoints such as membrane integrity and photosynthetic activity. Hutchinson *et al.* (1981) showed that there was a significant loss of Mn^{2+} and K^+ from *Chlamydomonas angulosa* within 6 hours after exposure to naphthalene. Loss of K^+ was more rapid and complete than the loss of Mn^{2+}. Cation loss was attributed to hydrocarbon-induced membrane damage. Heldal *et al.* (1984) reported that hydroperoxides and quinones were extremely toxic to *D. bioculata,* causing immediate mortality and decreased biomass without affecting growth rates. These products, including 1-naphthoic acid, appeared to destroy the cell membrane without influencing cell division or growth rate. In general, it is accepted that several classes of compounds, including acids, alcohols, and phenolic compounds, can cause membrane damage (Heldal *et al.*, 1984). Most breakdown products of petroleum hydrocarbons can be classified into one of these groups. These compounds appear to physically disrupt membranes by solublizing their lipid constituents, thus destroying the structure and function of the membrane (Heldal *et al.*, 1984). Other metabolites may exert membrane damage via highly unstable oxidative intermediates such as superoxide radicals. These highly reactive compounds may react directly with proteins or other membrane constituents which may lead to the destruction of the integrity of the membrane and result in swelling or lysis of the cell.

Photosynthesis inhibition is yet another endpoint that is typically measured in assessing petroleum hydrocarbon exposure. Several different products including naphthalene, whole crudes, WSFs of petroleum hydrocarbons, and coal liquefaction products have been shown to inhibit photosynthesis in *C. angulosa*, *Selenastrum capricornutum,* and *Anabaena doliolum* (Gaur and Singh, 1991; Giddings, 1979; Giddings and Washington, 1981; Soto *et al.*, 1975b). This decrease in photosynthetic activity can lead to a decrease in oxygen evolution and subsequent increases in carbon dioxide levels. The alteration of either of these gases, in turn, can have other environmental implications. The specific toxic mechanism for naphthoquinones and potentially other petroleum hydrocarbons is the inhibition of the electron transport chain at photosystem II (Lichtenthaler and Pfister, 1978). Although there are several different petroleum hydrocarbons that can inhibit photosynthesis, it appears the effects are not long-lasting, as the photosynthetic recovery rate of *C. angulosa* was inversely correlated with incubation time in closed systems with naphthalene and aqueous crude oil (Soto *et al.*, 1975b).

Secondary Effects. Although it has been shown that the majority of the nutrient supply from oil is due to the release of nutrients from heterotrophic activity, some studies have indicated that there is some degree of benefit directly from the assimilation of certain oil constituents in sterile conditions (Dogadina, 1970). However, it appears from the majority of studies that the favorable response of the algae is due to heterotrophic activity for two reasons. First, heterotrophs (cyanobacteria and bacteria) are generally less sensitive to petroleum hydrocarbons compared to algae (Table 4-4). Secondly, while populations of green algae typically decrease immediately after the spill, populations of blue-greens and bacteria increase almost immediately after exposure. For instance, cyanobacteria became the predominant species after exposure to aqueous extracts of No. 2 fuel oil by replacing the dominant diatom (Bott and Rogenmuser, 1978). Shifts in species composition were dependent upon oil source, as Nigerian crude neither altered species presence nor lowered biomass. Schindler *et al.* (1975) reported that the highest levels of Norman Wells crude oil (1%) produced the largest crops of algae. It was noted that populations of the nitrogen-fixing bacteria *Azotobacter* sp. were greatly increased and correlated with the increased nitrate levels. As there was no addition of any nitrogen to any of the ponds, it stands to reason that the increased levels of nitrate were due to *Azotobacter* utilization of the oil.

Substantial shifts in species compositions can result from the effects of oil spills. In a study by Schultz and Tebo (1975), 7,000 gallons of No. 2 diesel fuel were released into a South Carolina creek and several sites were monitored for changes in species composition for 6 months. Filamentous blue-greens were very common 2 to 3 months after initial exposure. However, by 6, months the treated sites were totally dominated by pennate diatoms, while the control site had a more equal representation of pennate and centric diatoms as well as blue-greens. This result suggests that there may be other impacts to the "health" of the system, such as alterations in community structure, not only in taxonomic shifts from autotrophs to heterotrophs but, also, in changes among different autotrophs. These alterations have the possibility of impacting community function, potentially resulting in other environmental ramifications.

Another indirect effect of algal dynamics resulting from oil spills is reduction of herbivore populations (Miller *et al.*, 1978). In general, zooplankton are more sensitive to petroleum hydrocarbons than are algae (see Table 4-6). Without the presence of predators and with an increased nutrient supply, algal populations can go unchecked and exceed original population numbers. This population increase can lead to an overproductive state which, in turn, can lead to decreased dissolved oxygen concentrations, causing negative impacts even after toxic effects have subsided (Werner *et al.*, 1985). Oxygen consumption was shown to rise up to 400% in microcosms exposed to South Louisiana Crude and Wyoming Crude in the dark. In systems with a 16:8 hour light:dark photoperiod, community metabolism shifted from balanced or net oxygen production to net oxygen consumption (Werner *et al.*, 1985). However, in areas with sufficient oxygen levels, there appears to be a positive interaction between the heterotrophic cyanobacteria and bacteria and the autotrophic green algae. Overall, it appears that algal populations are more sensitive to the secondary effects of oil pollution, such as oxygen consumption and nutrient release, compared to the more direct toxic effects.

Macrophytes

This is a generic term referring to aquatic plants other than microalgae. For the purposes of this discussion it will include shoreline submerged and emergent plants, floating vascular plants, and marsh and swamp plants with emergent shoots.

Some of the most obvious and extensive biotic effects of oil spills may be those on freshwater aquatic plants (Blundon *et al.*, 1987). Aquatic vegetation and shoreline wetlands typically serve critical ecological functions, providing nursery and protective habitat for estuarine organisms and terrestrial wildlife, protection against bank erosion, and water quality enhancement (Mitsch and Gosselink, 1986). Additionally, coastal and shoreline wetlands often are located in close proximity to areas of intensive oil production and transportation (e.g., along the river banks and swamplands of southern Louisiana and Texas). Consequently, oil spill impacts to aquatic macrophytes can be ecologically significant and may represent a principal area of concern in formulating spill-response strategies.

Unfortunately, only limited information is available on the effects of oils on aquatic plants, especially freshwater species. Data have primarily been collected from post-spill observational studies, and little is known regarding the mechanisms of hydrocarbon toxicity to plants. Prior reviews include Baker (1970), Baker *et al.* (1989), and Shales *et al.* (1989).

The degree of impact of spilled oil on freshwater macrophytes will tend to vary with several biotic and abiotic factors, including: the type and amount of oil spilled; the dynamics of water transport through the vegetated system; the plant species present; the extent of oil coverage of plant tissues; the extent of oil penetration into soil rooting zones; season; and soil composition (Burk, 1977; Mendelssohn *et al.*, 1990; Baker *et al.*, 1989; Lin and Mendelssohn; 1996). Petroleum hydrocarbons can affect plants via disruption of plant-water relationships (McCown and Deneke, 1972), interruption with nutrient uptake (Ibid.), toxicity to living cells (Prendevolle and Warren, 1977), and reduced oxygen transport into the soil rooting zone (Stebbing, 1970).

Effects of spilled oil on shoreline vegetation in moving water systems (rivers and streams) will tend to be less severe than those in standing water or very slow moving systems (lakes, ponds, marshes, and swamps). In rivers, spilled oil tends to adhere to, and adversely affect, primarily the outer fringing vegetation of shoreline stands; interior plants may be insulated from the effects of the oil (Baca *et al.*, 1983). River action tends to flush the oil from shoreline vegetation stands before it can reach inner plants and penetrate soil substrates. For this reason, and because fringing vegetation is important to controlling the erosion of river banks, the cutting of river bank oiled plant stems during cleanup operations may be counterproductive. Although spilled product can, thereby, be removed from the river, decreased bank stability and increased oil penetration to inner plant stems may result, impeding the recovery of shoreline vegetation (Baca *et al.*, 1985). Cutting may also directly impair the regrowth and recovery of oil-exposed plants. Baca *et al.* (1985) reported that cut marsh grass and sedges failed to survive a spill due to the exposure of roots and basal meristems to spilled oil.

Oil spills tend to be more devastating to standing water plant communities. Increased residence time of the oil allows for prolonged exposure to plant stems and penetration of oil into substrates (Burk, 1977; Baca *et al.*, 1985). Oil penetration into soils may result in a delayed toxic threat to rooted vegetation (Blundon *et al.*, 1987). If not redistributed by water action, oil on the surface of soils can weather to form a hardened crust (tarmac). This may inhibit plant growth and impede the emergence of new shoots (Baker *et al.*,1989).

Burk (1977) monitored the effects of an oil spill into a freshwater Massachusetts marsh. He found significant variation in the sensitivity of different marsh species to oiling, with perennials more resistant than annuals. Baca *et al.* (1985) observed similar responses following a crude oil spill into a Louisiana cypress swamp. One year following the spill, they found very few effects on woody vegetation, but significant effects on floating vascular vegetation. Areas of water in the swamp once covered by water hyacinth were devoid of any vegetation; however, perennials were returning in all sunlit areas of the swamp. Baker (1971) similarly reported greater survival of perennials in oil-polluted water. Perennial wetland species tend to be robust, with substantial underground reserves and natural winter die-back of above-ground tissues (Baker *et al.*, 1989), and have been shown to recover well from light to moderate, and sometimes multiple, oilings (Id.).

Lin and Mendelssohn (1996) compared the oil-induced responses of two salt marsh grasses (*Spartina alterniflora* and *Spartina patens*) with that of a freshwater marsh grass (*Sagittaria lancifolia*). They found that the generally greater stress tolerance of salt marsh plants did not extend to oil impacts. *S. lancifolia* was shown to be oil resistant at exposure rates of up to 24 liters of south Louisiana crude oil per meter of marsh sod. Growth of this species was actually stimulated by the application of the oil. In contrast, the *Spartina* species were adversely affected. Photosynthesis, plant stem density, and plant biomass were reduced significantly, relative to controls, in plants exposed to oil at concentrations ranging from 4 to 24 L/m^2. The reductions in stem density were assumed to be caused either by the lethal effect of floating oil on newly growing tillers or by the effect of oil that had penetrated the soil on the generation of new tillers.

S. lancifolia shoots were apparently resistant to exposure to south Louisiana crude oil and were able to penetrate surface oil without injury (Lin and Mendelsohn, 1996). Other freshwater species, however, including *E. quadrangulata*, *C. odoratus*, and *A. teres*, did not exhibit resistance to oiling similar to *S. lancifolia.* They either were killed or suffered reduced growth at oil exposure concentrations of 4 to 8 L/m^2. These results suggest that *S. lancifolia* may be useful for re-vegetating oil-damaged freshwater wetland systems (Lin and Mendelssohn, 1996). Baker *et al.* (1989) reported that the reed, *Phragmites australis,* is also highly tolerant of oiling. It was observed growing, although in a stunted state, in soils containing up to 57% heavily weathered oil. Good growth was reported for plants growing where the soil oil concentration was 20%. Baker's results suggest that a number of tolerant wetland plant species can recover from oilings and can tolerate a certain amount of hydrocarbons in the soil (Baker *et al.*, 1989).

Lin and Mendelssohn (1996) attributed observed patterns in oil sensitivity among plant species, in part, to soil organic content and soil texture. Organic matter in soil was found to be the primary factor controlling oil penetration into soil. More organically enriched soils contained higher concentrations of oil following long-term exposures. Coarser soils also tended to show higher oil penetration. Plants growing in highly organic and/or coarse soils, therefore, will tend to suffer more severe effects than plants in unenriched soils due to greater oil exposure of rooting tissues.

Other freshwater plant species sensitivity comparisons were reported by Blundon *et al.* (1987). They exposed sedge, sphagnum moss, sandbar willow, reindeer lichen, and black spruce to Norman Wells crude alone and combined with two dispersants (Corexit 7664 and 9600). Oil was poured onto soil substrates and sprayed onto foliage. Lichen and sedge were the most tolerant species; moss and black spruce suffered the greatest effects. Oil poured onto the soil caused greater defoliation than oil sprayed onto the foliage, suggesting that effects of root exposure to hydrocarbons may predominate over those due to above-ground plant tissue exposure. Sedges were the only species to show good recovery approximately two months after oil exposure. These results are consistent with those reported by Wein and Bliss (1973). They found that oil eliminated mosses from arctic wetland spill sites, but that sedge species showed good post-spill recovery.

The physiological effects of oiling on macrophytes have not been extensively studied. Oiling may reduce rates of photosynthesis, either by modifying the permeability of cell membranes or by reducing light assimilation by chloroplasts (Baker, 1970). Oil may reduce transpiration rates through blocking of stomata. Other observed effects of oiling on macrophytes include damage to cell membranes, inhibition of translocation, and even increased respiration rates (Boyles, 1967). The macrophyte's form, growing habitat, thickness of cuticle, leaf structure and permeability, and growth/reproductive stage are factors that may affect the vulnerability of various macrophytes to oil.

Oil may pose adverse effects to macrophytes by inhibiting seed germination. Oil may penetrate the seed and cause toxicity to the embryo, or it may coat the seed and cause oxygen deprivation and reduced water uptake (Cowell and Baker, 1969). Amakiri and Onofegharaf (1984) noted a decrease in germination of *Zea mays* coated with crude oil; however, they noted no effect on *Capsicum frutenscens*.

Because of the attention paid to macrophytes during spill cleanup efforts, more information would be beneficial on their resiliency to cutting of oiled leaves and stems. It has been observed that heavy cutting can kill plants. In addition, plants with high tolerances to hydrocarbon exposures could be used beneficially after a spill to stabilize shorelines and lessen erosion where cutting was performed on oiled vegetation.

Invertebrates

Aquatic invertebrates typically comprise the greatest abundance of animals in freshwaters, occupying different trophic levels within the freshwater community. Because of this, they represent various important niches in the freshwater ecosystem, affecting ecosystem structure and function. Some invertebrates feed on plants, algae, or detritus, whereas others are typically carnivorous, feeding on other invertebrates and small vertebrates. Still other invertebrates overlap both of these classifications and are omnivorous (e.g., crayfish, isopods), or their feeding habits may change during their developmental life stage (e.g., blackflies).

Overall invertebrates provide a vital energy link between primary producers (e.g., algae) and tertiary consumers higher in the trophic food level (e.g., insectivorous fish).

Oil spills may impact aquatic invertebrates directly or indirectly. Alterations to the invertebrate community caused directly by the oil include acute lethal toxicity, sublethal toxicity (e.g., reduced reproduction), or physical impairment/entrapment. Indirect environmental effects include changes such as reduced dissolved oxygen, which may lead to a reduction of suitable habitat or food supply.

Acute Lethal Toxicity. In general, invertebrates are moderately sensitive to petroleum hydrocarbons compared to other aquatic organisms (Table 4-4); their LC_{50}s are typically lower than those for algae, but equal to or higher than those for fish. Studies comparing the relative sensitivities of several invertebrates to an arbitrary reference mixture (ARM) of refinery wastes (reported as fractions of the ARM) indicated that water fleas (i.e., daphnids) were the most sensitive (48-hour LC_{50} 0.06 mg/L), followed by first instar mosquito larvae (0.5-0.8 mg/L), planaria (2.0 mg/L), and amphipods (3.2 mg/L) (Buikema *et al.* 1976). Crayfish, snails, and worms were generally less sensitive.

O'Brien (1978) concluded that arctic zooplankton in general were the most sensitive invertebrates to Prudhoe Bay crude oil. Laboratory and field experiments confirmed that fairy shrimp were the most sensitive, followed by *Daphnia*, while cyclopoid copepods appeared to be fairly resistant to the effects of oil. Fairy shrimp populations were severely impacted within 24 hours following a simulated oil spill (240 ml/m^3) of Prudhoe Bay crude oil into an experimental pond, and were completely wiped out within 48 hours . Daphnids were completely decimated by four days after initial exposure, and one species of copepod (*Heterocope septentrionalis*) was eliminated after six days. Another species of copepod (*Cyclops* spp.) appeared to be unaffected by oil exposure.

Additional field experiments indicated that caddisflies and stoneflies are selectively eliminated after exposure to Prudhoe Bay crude oil at 10 and 0.24 ml/L (Mozley and Butler, 1978). Chironomids (midge larvae), typically regarded as insensitive species, were not eliminated after similar exposure, but their emergence rates were significantly reduced. Chironomids in the Orthocladiinae tribe increased in abundance following exposure, while chironomids in the tribe Tanytarsini were greatly reduced. There was no recovery of caddisflies, stoneflies, or Tanytarsini seven years after exposure to crude oil (Mozley and Butler, 1978). Other studies have found that certain species (*Agrion* [Odonata], *Dugesia* [Turbellaria] and *Gammarus* [Amphipoda]) were eliminated from stretches of a stream with oiled sediments, whereas Tubifex (Oligocheata), *Chironomus* (Diptera), Nematoda and Hirudinea (Annelida) persisted (McCauley, 1966; Mozley and Butler, 1978).

Sub-lethal Effects . Full strength diesel fuel oil WSF did not have lethal effects on two species of adult freshwater snails, although as low as 8% and 32% WSF reduced hatching (Milleman *et al.*, 1984b).

It appears that organisms respond to oil constituents differently. For instance, the WSFs of creosote and phenanthrene reduced growth rates, the number of broods, and molting, while increasing the number of aborted young for *D. pulex*. Number 2 fuel oil affected daphnids similarly, although results were less significant. In contrast, the only effect of naphthalene WSFs was a slight reduction in growth rate (Geiger and Buikema, 1982). Chronic exposure of freshwater prawn (*Macrobrachium lamerrii*) to diesel resulted in a decrease in the ovarian index and egg diameter, and also resulted in morphological changes to the ovaries due to degeneration (Rao *et al.*, 1990).

The filtering rates of *D. pulex* were significantly increased by exposure to either the LC_{20} or LC_{30} (the concentration of material in air expected to cause mortality in 20% and 30% of a population, respectively) of creosote and No. 2 fuel oil, but were basically unaffected by either phenanthrene or naphthlene. Both fresh and weathered Norman Wells crude oil were shown to interfere with feeding behavior and prey capture efficiency for the planktonic rotifer, *Asplanchna sieboldi* (Rogerson *et al.*, 1982).

Crider *et al.* (1982) demonstrated that oxygen consumption of *D. magna* decreased during exposure to naphthalene. They further observed decreased hemoglobin concentrations with increased naphthalene concentrations. The primary cause of decreased oxygen consumption was hypothesized to be the inhibition of the electron transport system by naphthalene. Other studies have demonstrated that exposure to the LC_{20} or LC_{30} of naphthlene, phenanthrene, No. 2 fuel oil, and creosote WSFs individually did not affect respiration rates of *D. pulex* (Geiger and Buikema, 1981).

Uptake, Metabolism, and Excretion of Petroleum Hydrocarbons. Most of the uptake/elimination studies have focused on zooplankton species, as they tend to be more susceptible to petroleum products (O'Brien, 1978). The majority of petroleum hydrocarbons are readily available for uptake from water by freshwater invertebrates. This is mainly due to their general hydrophobic as well as lipophilic nature, but uptake is specific for the individual constituents (see Tables 3-7 and 3-10). Studies assessing the accumulation of radiolabeled hydrocarbons (including benzene, naphthalene, phenanthrene, benzo(a)anthracene [BaA], and benzo(a)pyrene [BaP]), from food and water for the zooplankter, *Daphnia pulex*, indicated that uptake depends on the vector of exposure and the individual compound (Trucco *et al.*, 1983). *D. pulex* accumulated naphthalene the greatest in a 24-hour period from dietary exposure (11,000 x), while the accumulation of BaA and BaP were greater from aqueous exposure (1,000 and 3,000 x, respectively). Aqueous and dietary exposure of hydrocarbons in combination did not significantly influence uptake rates versus exposure to either individually. Of all five aromatic hydrocarbons tested, benzene was accumulated the least by *D. pulex*, although there was no difference between dietary and aqueous uptake for either benzene or phenanthrene (Trucco *et al.*, 1983). BCFs for BaP were similar, ranging from 3,000 to 8,000 using *D. magna* (McCarthy, 1983; Leversee *et al.*, 1983). BCFs for other PAHs were somewhat lower; 607 for anthracene, 968 for dimethylbezanthracene, 667 for methylcholanthrene, and 652 for dibenzanthracene. The BCF for anthracene using the amphipod, *Hyalella azteca*, was empirically determined to be 1800 (Landrum and Scavia, 1983).

While it is apparent that aquatic invertebrates readily uptake petroleum hydrocarbons, several factors influence their bioavailability, including particulate organic matter, pH, and mode of exposure. The presence of particulate organic matter decreased the bioavailability of some PAHs up to 97% (McCarthy, 1983), although this decrease may be dependent on the specific

PAH and the type of organic matter present (Leversee *et al.*, 1983). Other research has indicated that the bioaccumulation of pyrene was pH-dependent, showing lower uptake rates at lower pHs (Wildi *et al.*, 1994). Method of exposure is also an important consideration, as uptake rates may vary among different vectors. While the accumulation of certain petroleum hydrocarbons is influenced by dietary exposure (Trucco *et al.*, 1983), Landrum and Scavia (1983) reported that sediment associated anthracene contributed 77% of the total body-burden for *H. azteca*. This suggests that epibenthic organisms may be at the greatest risk from petroleum products compared to other organisms.

Although certain oil constituents, like BaP, may be accumulated at higher rates than others (e.g., naphthalene), depuration rates for these compounds are generally elevated as well. For instance, *D. pulex* depurated approximately 85% of accumulated hydrocarbons (including BaP) within a 72 hour period, although naphthalene was depurated to only 30% of the original concentration (Trucco *et al.*, 1983). Depuration half-lives for several PAHs varied between 0.4-0.5 hour using *D. pulex* (Eisler, 1987). Studies have shown that midge larvae depurated 72% of BaP in 8 hours, while daphnids depurated 21% in 18 hours (Eisler, 1987). Amphipods eliminated approximately 30% of anthracene within eight hours, although the presence of sediment increased depuration by a factor of three (Landrum and Scavia 1983). It appears that, for the majority of freshwater invertebrates, depuration rates for large molecular weight compounds (e.g., BaP) are high. These high rates are due to the organism's ability to quickly metabolize or excrete these compounds.

While the cytochrome P-450-dependent mixed-function oxidase is responsible for initiating the metabolism of various lipophilic compounds for most vertebrates, the comparable enzyme system responsible for this metabolism in invertebrates is less understood. However, MFO activity does appear to exist for certain invertebrates, including members of the phyla Arthropoda and Annelida (Neff, 1985). Both the hepatopancreas and the green gland of the red swamp crayfish (*Procambarus clarkii*) have been shown to metabolize BaP, producing a number of the same metabolites as vertebrate enzyme systems (Jewwell *et al.*, 1989). As with the vertebrates, the adaptation of cytochrome P-450 enables organisms to excrete more lipophilic compounds by producing more hydrophilic metabolites. However, as with the vertebrates, MFO metabolism of certain PAHs can result in the formation of certain toxic intermediates, arene oxides, that may covalently bind to genetic material such as DNA, RNA, and protein. While certain invertebrates appear to have other enzymes capable of metabolizing PAHs, like epoxide hydratase and aldrin expodiase (Neff, 1985), invertebrate enzymes' activity, specific location, specificity to different compounds, and degree of prevalence among different classes of invertebrates vary or are largely unknown.

Ecological Effects. Because of the important role invertebrates play in the freshwater ecosystem, it is easy to understand the potential environmental ramifications of a freshwater oil spill. Oil spills may affect organisms directly or indirectly; direct alterations to the community include acute lethal toxicity, sublethal toxicity (e.g., reduced reproduction), or physical impairment/entrapment, while indirect environmental effects include changes such as reduced dissolved oxygen, which may lead to a reduction of suitable habitat or food supply. However, oil impacts to most primary producers (e.g., algae and plants) are not as severe nor as long lasting as they are to invertebrates or vertebrates (see appropriate sections). Thus, indirect effects from decreased food supply are not thought to be a major stressor to invertebrates from oil spills. On the other hand, delayed recovery of invertebrate populations in the face of recovering algal populations may lift grazing pressure on the algae. Assuming the algae are not nutrient or otherwise limited, this may lead to algal blooms or increased lake eutrophication.

Freshwater oil spills can result in a large decrease in overall invertebrate density, number of taxa, and standing crop (Crunkilton and Duchrow, 1990; Harrel, 1985). Almost all organisms can be effected by oil, but the extent of effects is dependent on the type and volume of oil, among other factors. Typically, the first organisms to be eliminated after a spill include certain species of crustaceans and insects, often referred to as indicator organisms. These indicator species include cladocerans (e.g., *Daphnia* spp.), amphipods (e.g., *Hyalella azteca*), eubranchiopods (e.g., fairy shrimp), mayflies, stoneflies, and caddisflies. Daphnids, amphipods, and fairy shrimp tend to be more dominant in lentic environments (stationary waters, e.g., ponds) while mayflies, stoneflies, and caddisflies are usually more dominant in lotic environments (running waters).

The post-spill community is usually dominated by certain species of organisms that are generally regarded as being more tolerant to stressors, including chironomids (midges), simulids (blackflies), oligochetes (segmented worms), and gastropods (snails) (Crunkilton and Duchrow, 1990). While certain groups within the chironomids are very tolerant of oiled areas (i.e., Orthocladiinae), others are relatively sensitive (i.e., Tanypodinae and Chironominae) (Rosenberg and Wiens, 1976). Aquatic invertebrates in lotic environments, especially insects, have also been observed trying to avoid freshwater oil spills by drifting (Miller *et al.*, 1986).

Fish

Because of their commercial and recreational value, fish impacted by oil spills tend to receive greater attention than other organism populations. Standardized laboratory testing methods tend to be better developed with respect to fish species than many other animal or plant groups. Fish may be affected both as a direct result of the physical properties of oil and from the toxicity of dissolved or dispersed oil. Spilled oil will tend to disrupt surface feeding, may coat and irritate gill membranes, and will be variably toxic to differentially sensitive fish species. Obviously, there is a greater potential for adverse effects on fish in confined waters (i.e., lakes and ponds), as opposed to flowing, freshwater systems.

Accumulation, Metabolism, and Excretion of Petroleum Hydrocarbons. Petroleum hydrocarbons, especially aromatics, are readily taken up by fish. Berry (1980) exposed bluegill sunfish to solutions containing radiolabeled toluene and observed that toluene concentrations in bluegill reached a steady state after only 24 hours of exposure. The highest concentrations of toluene and radiolabeled metabolites in tissues, about 50 times higher than those in water, occurred in the spleen, gall bladder, heart and testes. Similar patterns were observed for naphthalene in American eel after ingestion of crude oil (Nava and Engelhardt, 1980).

Klein and Jenkins (1983) measured the uptake of hydrocarbons from the WSF of JP-8 jet fuel. Bioconcentration factors (BCFs, ratios of concentrations in tissue to concentrations in water) were 160 for American flagfish and 63 to 112 for rainbow trout. Uptake of mono- and diaromatics from dispersions of Wyoming crude oil resulted in BCFs of 150 to 450 in cutthroat trout (Woodward *et al.*, 1981). The BCFs for naphthalene and 2-methylnaphthalene ranged from 40 to 300 in rainbow trout (Melancon and Lech, 1978).

Aromatics are metabolized in the liver through the action of mixed function oxidases (MFOs). The resulting metabolites are generally more soluble and, therefore, more easily excreted, than the parent compounds. The metabolites accumulate in bile in the gall bladder, from which they are excreted through the gut (Berry, 1980; Rice, 1985). MFO activity is present at low levels in unexposed fish, but increases rapidly as a compensatory response upon exposure to an appropriate substrate, such as PAH. Nava and Engelhardt (1982) measured increases in activity of MFO, and specifically benzo(a)pyrene hydroxylase (an aryl hydrocarbon hydroxylase, or AHH), in the livers of eels three days after ingestion of crude oil. There was no consistent relationship between oil exposure level and AHH activity. Vandermeulen (1990) observed a threshold response in AHH induction in brook trout under experimental slicks of Bunker C, No. 2 fuel oil, and Kuwait crude. Low levels of exposure caused no induction, but when exposure exceeded a certain threshold, AHH activity increased. Further increases in exposure resulted in no increase in AHH activity, consistent with the results of Nava and Engelhardt (1982). The threshold hydrocarbon concentration for AHH induction varied with the aromaticity of the three oils, lowest for Bunker C (most aromatic) and highest for No. 2 fuel oil (least aromatic). Induction of MFO or AHH activity has also been observed in coho salmon exposed to crude oil WSF (Thomas *et al.*, 1989) and in rainbow trout exposed to dispersions of No. 2 fuel oil (Steadman *et al.*, 1991a).

Though MFO induction is presumably a beneficial adaptation, enabling organisms to detoxify and eliminate a wide variety of toxicants, it carries a physiological cost. MFO enzyme synthesis, manifested as an increase in liver protein requires energy (Nava and Engelhardt, 1982; Vignier *et al.*, 1992). Exposure to oil is often accompanied by an increase in liver weight (Steadman *et al.*, 1991a; Vignier *et al.*, 1992) and may be associated with a decrease in overall growth (Hedtke and Puglisi, 1980; Engelhardt *et al.*, 1981; Woodward *et al.*, 1981; Rice, 1985; Vignier *et al.*, 1992). Other indicators of liver metabolic responses to hydrocarbon exposure include higher concentrations of reduced glutathione (Steadman *et al.*, 1991a), changes in liver fatty acid composition (Rice, 1985), and decreases in liver glycogen and lipids (Hawkes, 1977;

Vigner *et al.*, 1992). Also, MFO metabolites are not always more soluble and less toxic than the aromatic parent compounds. The metabolites can be more persistent, and some (e.g., epoxides) are toxic, carcinogenic, and teratogenic (Rice, 1985). Stüber and Zahn (1985) detected DNA damage as well as increased liver MFO activity in rainbow trout three months after exposure to a kerosene spill.

While most of the attention of researchers has been directed toward metabolism of aromatics by MFOs, fish can also metabolize and excrete saturated hydrocarbons. Rainbow trout fed a diet containing dodecylcyclohexane (a naphthene) and pristane (a branched alkane) accumulated both compounds in adipose tissue (Cravedi and Tulliez, 1982). Steady state was reached for dodecylcyclohexane in 3 months and for pristane in 6 months. These long periods to reach equilibrium (aromatic concentrations in tissues reach steady state in a matter of days) imply relatively slow rates of depuration. When the fish were switched to a clean diet, both compounds were gradually eliminated (about 40% reduction in 2 months).

Histopathology. A fundamental toxicological effect of petroleum and petroleum constituents is disruption of cell membranes. This disruption leads to impairment of osmoregulation which, in turn, causes a variety of effects on the structure and function of fish gills and blood chemistry.

At low levels of exposure to oils, the gill epithelial cells take on water and the mucous cells in the gill epithelium become enlarged (Prasad, 1988, 1991). The increased mucous production helps protect the gills from direct contact with the oil, and may improve osmoregulation, but it also may interfere with gas exchange and lead to asphyxiation. At higher levels of exposure, lesions occur in the gill epithelium (Hawkes, 1977; McKeown and March, 1978; Hedtke and Puglisi, 1980; Engelhardt *et al.*, 1981; Woodward *et al.*, 1981; Rice, 1985; Prasad, 1988, 1991). Eye lens tissues are also susceptible to damage from oil (Hawkes, 1977; Payne *et al.*, 1978; Engelhardt *et al.*, 1981; Woodward *et al.*, 1981).

Effects on the blood indicative of impaired osmoregulation include changes in serum ions, especially sodium, potassium, and chloride (Engelhardt *et al.*, 1981); decreased serum glucose (McKeown and March, 1978); increased plasma cortisol (Engelhardt *et al.*, 1981); decreased hemoglobin (McCloskey and Oris, 1993); and suppressed serum lysozyme level (Tahir and Secombes, 1995).

Osmoregulation is especially important for anadromous fish, which migrate from fresh- to saltwater and back again during their life cycle. Moles *et al.* (1979) measured the toxicity of the WSF of Prudhoe Bay crude oil on juvenile Dolly Varden, sockeye salmon, and pink salmon collected as they were migrating to the ocean. These fish, which had spent their entire development in freshwater but were now ready to move to saltwater, were twice as sensitive to the WSF in saltwater as in freshwater due to the stress of osmotic acclimation.

Effects on Reproduction and Embryo Survival. It is not surprising that effects of oils on fish metabolism and growth, and physiological and histological damage caused by impaired osmoregulation, can lead to reduced reproduction and survival. Tilghman-Hall and Oris (1991) observed decreased egg production, reduced hatching success, reduced larval survival, and teratogenic effects in fathead minnows exposed to anthracene for six weeks. American flagfish exposed to dispersions and WSFs of used crankcase oil produced fewer eggs than controls, though no effects were observed on hatchability or larval survival (Hedtke and Puglisi, 1980). Exposure to oil interferes with yolk absorption and growth of newly hatched cutthroat trout (Woodward *et al.*, 1983) and rainbow trout (Cotto Ramusino *et al.*, 1984).

Effects on Behavior. Fish exposed to oils exhibit a typical pattern of behavioral changes (Engelhardt *et al.*, 1981; Woodward *et al.*, 1983; Cotta Ramusino *et al.*, 1984; Steadman *et al.*, 1991b). The first symptoms are “restlessness,” overexcitability, and increased respiration rate. Fish that normally remain near the bottom begin swimming near the surface, and eventually lose equilibrium. These effects are reversible when the fish are removed to clean water. Advanced symptoms include fin paralysis, immobilization, and finally death.

Fish can detect and avoid relatively low concentrations of oil components. Rice (1985) states that fish can detect hydrocarbons at approximately one percent of the LC_{50} concentration. The threshold for avoidance of fluoranthene by fathead minnows is between 8.6 and 14.7 µg/L, near the threshold for subacute effects on larvae (Farr *et al.*, 1995). Embryos and larvae are unable to avoid oil exposure, which contributes to their susceptibility to effects of spills (Rice, 1985).

Though exposure to oil (JP-4) has been observed to cause lesions of the olfactory mucosa of fathead minnows (Latendress and Fisher, 1983), the ability of coho salmon to detect their home source water was unaffected by exposure to Prudhoe Bay crude oil (API, 1986; Nakatani *et al.*, 1987).

Examples of Effects of Freshwater Oil Spills on Fish. Reported effects of oil spills on fish are summarized in Table 4-10, and details are presented below. Extensive mortality has occurred in some cases (e.g., Schultz and Tebo, 1975; Alexander *et al.*, 1981; Guiney *et al.*, 1987a; Crunkilton and Duchrow, 1990), while in other cases little or no effect has been observed (e.g., Masnik *et al.*, 1976; Michaelis, 1983; Neff *et al.*, 1995). Factors influencing the severity of effects include the nature of the oil, the volume spilled, and the location of the spill. Even when major fish kills have occurred, populations have often been observed to recover within months, and long-term changes in fish abundance have not been reported (Schultz and Tebo, 1975; Alexander *et al.*, 1981; Guiney *et al.*, 1987a; Neff *et al.*, 1995).

- Gatun Lake, Panama Canal. Chong *et al.* (1983) described the response to a spill of an estimated 168,000 gallons (650,000 liters) of Alaska North Slope crude. Few fish were found dead and no reports of dead fish were received from sports fishermen in the area.

- Asher Creek, Missouri. Crunkilton and Duchrow (1990) described the impacts of a 400,000 gallon (1.5 million liter) crude oil spill. 42,000 fish were killed in an 8-km reach downstream from the spill.

- Newton Lake, Illinois. Effects of a spill of 453,000 gallons (1.8 million liters) of Southern Louisiana crude oil into a 1750-acre power plant cooling lake were assessed by Neff *et al.* (1995). About 200 fish were killed immediately after the spill. A small decrease in abundance of largemouth bass and white crappie was noted that summer, though it could not be definitively attributed to the oil spill. No apparent effects on the fisheries occurred for the next five years.

- Hayford Creek, California. Bury (1972) summarized the effects of a spill of approximately 2,000 gallons (9,000 liters) of diesel fuel into Hayford Creek, a stream consisting of a series of pools with connecting riffles. More than 2,500 fish of four species (lamprey ammocoetes, suckers, speckled dace, and rainbow trout) were killed.

- Boone Creek, South Carolina. A six-month biological survey was performed to study the effects of a 7,000 gallon (26,500 liter) spill of No. 2 diesel fuel (Schultz and Tebo, 1975). The oil was lethal to approximately 90% of the standing crop of fish. Six months later, recovery of the fish populations was apparent; species collected at a reference site were found at the oiled sites, and yellowfin shiners were found at all stations.

- Plum Creek, Virginia. The effects of a spill of 34,000 gallons (133,000 liters) of No. 2 diesel fuel on the biota of Plum Creek, southwestern Virginia, were studied by Hoehn *et al.* (1974) and Masnick *et al.* (1976). Eight dead fish were found within one day of the spill, but over the four month survey period, the diversity and total numbers of fish did not decrease.

- Durbin Creek, South Carolina. A ruptured pipeline released approximately 546,000 gallons (2.1 million liters) of No. 2 fuel oil into Durbin Creek in December 1991 (Smith, 1993). All but 62,000 liters were recovered. The South Carolina Wildlife and Marine Resources Department reported that 2,123 fish, representing 24 species, were killed along nine miles of Durbin Creek.

- Monongahela River, Ohio. The Ashland spill of January 1988, near Pittsburgh, was one of the largest inland spills in the United States. The spill is described by Laskowski and Voltaggio (1989), Miklaucik and Saseen (1989), and Frink and Dalton (1989). A collapsing storage tank released 3.8 million gallons of No. 2 diesel fuel, of which an estimated 750,000 gallons (2.8 million liters) entered the Monongahela River. Some of this oil became dispersed throughout the water column. Numerous dead fish were observed following the spill (Lemonick, 1988). Most fish mortality occurred in a river pool near the spill site in which diesel oil in water reached concentrations of 0.6 to 0.7 mg/L; however, it was estimated that mortality there was less than 10% of the fish population. Fish caught within 200 miles downstream contained elevated levels of naphthalenes, but no concentrations that posed a risk to human health (Berkey *et al.*, 1988).

- Roaring Run and Howell's Run Creeks, Pennsylvania. Guiney *et al.* (1987a) monitored the effects from a 55,000 gallon (208,000 liter) spill of aviation kerosene into a fast-flowing mountain stream. A complete fish kill occurred for at least 6.5 km downstream from the site. Recovery had largely taken place after seven months. Within a year, young-of-the-year minnows and sunfish were found, indicating that the streams were again suitable for breeding. Elevated concentrations of hydrocarbons, however, were detected in sediment samples and tissues of fish collected up to 14 months after the spill occurred (Guiney *et al.*, 1987b).

- Wolf Lodge Creek, Idaho. A pipeline break released 25,000 gallons (94,000 liters) of unleaded gasoline into Wolf Lodge Creek, a highly valued spawing site for cutthroat trout in northern Idaho (Graves, 1985). The spill killed many fish in the main channel of the creek, and no fish were found there 17 days after the spill.

- Lake Winona, Minnesota. Fremling (1981) described a spill of about 7,400 gallons (29,000 liters) of No. 6 fuel oil into Lake Winona, Minnesota. The discharge, which occurred in winter via a storm sewer, was undetected until April because of ice cover. Though most of the surface oil was recovered, globules of heavy oil continued to rise from the lake bottom during the summer. From 6 to 10 weeks after the spill was noticed, an estimated 190,000 bluegill sunfish and a few crappies were found dead. Fremling (1981) concluded that the spill stressed spawning bluegill sufficiently to trigger a kill by *Flexibacter columnaris* bacteria.

- Columbia River, Washington and Oregon. Blahm *et al.* (1980) described the effects of a spill of 30,000 to 58,000 gallons (113,550 to 219,520 liters) of Bunker C into the Columbia River near Portland, Oregon. Fish catches using several methods were compared from before and after the spill to assess the impact. For a few days after the spill, no fish were collected in catches. Trawl catches before the spill were low, but afterwards only half the number of species were collected. At the trawling stations immediately below the spill site, the number of species dropped from five (Pacific lamprey, white sturgeon, western speckled dace, coast range sculpin, and coho salmon) before the spill to only one (white sturgeon) afterwards.

Purse seining in the area immediately below the spill indicated a drop from seven species (Pacific lamprey, coho and sockeye salmon, spring and fall chinook, steelhead, and peamouth) before the spill to three species (coho, fall chinook, and peamouth) after the spill. The total number of fish dropped from 457 to 84. About 50 km downstream, seven species (American shad, largescale sucker, staghorn sculpin, white sturgeon, peamouth, prickly sculpin, and starry flounder) were found before the spill, but only the latter four were found afterwards; total numbers of fish dropped from 286 to fewer than 20.

- Delaware River, Delaware. On June 24, 1989, an Uraguayan tanker *Presidente Rivera* grounded and spilled 300,000 gallons (1.13 million liters) of No. 6 oil on the Delaware River (Wiltshire and Corcoran, 1991). River temperatures were lower than the pour point of the oil and much of the heavy oil formed globs that submerged. However, the spill occurred in the center of a striped bass nursery only six weeks after the prime spawning period, there was a minimal impact on fish. Weisberg *et al.* (1990) studied the effects of the spill on young-of-the-year striped bass by placing hatchery-reared, six-week-old striped bass in cages moored in the river five days after the spill. Greater than 90% survival was found at all stations after four days of exposure, and at all stations except one after 13 days of exposure (71% of the fish survived at the one exceptional station). Histopathological analysis of the exposed fish indicated no effects from the oil.

- St. Lawrence River, Canada. An estimated 307,000 gallons (17 million liters) of No. 6 fuel oil were spilled from the barge *Nepco 140* in June 1976 (Alexander *et al.*, 1981). Heavy mortalities of fish, as well as frogs, turtles, birds, and muskrats, were observed (Palm, 1979). Reduced numbers of larval fish were found in heavily oiled areas the following year.

Production of young largemouth bass declined in the oiled areas in 1977, but no effects were evident by 1978. Rock bass, black crappie, and bluegill showed no trend associated with oiling (Alexander *et al.*, 1981).

Table 4-10. Summary of effects of oil spills on fish.

Oil	Volume Spilled	Location	Effects on fish	Reference
Crude oil	650,000 L	Lake, Panama	Few dead fish	Chong *et al.*, 1983
Crude oil	1.5×10^6 L	Stream, Missouri	42,000 killed in 8-km reach	Crunkilton and Duchrow, 1990
Crude oil	1.7×10^6 L	Lake, Illinois	200 killed immediately; no long-term effect on abundance	Neff *et al.*, 1995
Diesel	9,000 L	Stream, California	2,500 killed 1.6 to 4 km downstream	Bury, 1972
Diesel	32,000 L	Stream, South Carolina	90% kill, recovery after 6 months	Schultz and Tebo, 1975
Diesel	133,000 L	Stream, Virginia	No effect	Masnik *et al.*, 1976
Diesel	2.1×10^6 L	Stream, South Carolina	2,000 killed in 15-km reach	Smith, 1993
Diesel	66×10^6 L	River, Pennsylvania	Many dead fish observed; <10% mortality	Lemonick, 1988; Berkey *et al.*, 1988
Aviation fuel	19,000 L	Stream, Oklahoma	2,600 killed in 3.2-km reach	Bugbee and Walter, 1973
Aviation kerosene	1310 barrels	Stream, Pennsylvania	Complete kill for 6.5 km; recovery in 6 months	Guiney *et al.*, 1987a
Gasoline	94,000 L	Stream, Idaho	Many fish killed	Graves, 1985
Bunker C	29,000 L	Lake, Minnesota	190,000 dead from bacterial infection	Fremling, 1981
Bunker C	220,000	River, Oregon	Reduced numbers, diversity for 50 km	Blahm *et al.*, 1980
Bunker C	1.13×10^6 L	River, Delaware	Minimal impact	Wiltshire and Corcoran, 1991
Bunker C	17×10^6 L	River, Ontario	Heavy mortality, no long-term effect	Alexander *et al.*, 1981
Unknown	17,000 L	Stream, New Zealand	No mortality of brown trout, eels	Michaelis, 1983

Amphibians and Reptiles

Amphibians and reptiles occupy both aquatic and terrestrial habitats. They may be exposed to toxic concentrations of petroleum constituents dissolved in the water column or may suffer from physical coating of floating or shoreline oil. Amphibians have permeable skin, respire across body surfaces, and are fully aquatic as larvae; therefore, they will tend to be more susceptible than reptiles to the water soluble fractions of spilled oil products. The primary risks of spilled oil to semi-aquatic reptiles (e.g., snakes, crocodiles, alligators, turtles) will be physical coating, ingestion, food depletion, and habitat destruction.

Hydrocarbon Toxicity. Very few studies have investigated hydrocarbon toxicity to reptiles and amphibians. Hedtke and Puglisi (1982) exposed wood frog larvae, spotted salamanders, and two warm water fish species (fathead minnows and American flagfish) to five oils (waste oil, kerosene, No. 2 fuel oil, mixed blend sweet crude oil, and Lloydminister crude oil) introduced as floating oil, an oil-water emulsion, and a water soluble fraction. Emulsions caused the most severe effects on test organisms. LC_{50} values were generally lower for frog larvae than for fish. However, frogs were tested at a lower temperature, perhaps accounting for the greater apparent sensitivity. Comparative toxicity data for frog larvae and salamanders were available only for No. 2 fuel oil as an emulsion, salamanders (LC_{50} = >86.4 µL oil/L water) appeared less sensitive than the frogs (LC_{50} = 4.9 µL oil/L water).

Hefler and Blankenmeyer (1990) found that naphthalene at 4.4 mg/L increased the transport of sodium across frog skin. This transport may represent a mechanism of petroleum toxicity to aqueous-exposed amphibians. Oil-in-water toxicity data are essentially unavailable for reptiles.

Observed Effects on Reptiles and Amphibians. Post-freshwater oil spill investigations have reported severe effects on exposed reptiles and amphibians. Large numbers of dead or stressed larval frogs, garter snakes, water snakes, and pond turtles have been observed following spill events (Bury, 1972; Meynell, 1973; Masnik *et al.*, 1976; Palm, 1979; and Alexander *et al.*, 1981). Interestingly, Masnik *et al.* (1976) observed high mortality of water snakes following a No. 2 fuel oil spill into a small freshwater stream, but found minimal effects on benthic or fish species.

Birds and Mammals

Few investigations have focused specifically on the effects of oil spills on birds and mammals inhabiting freshwater habitats. However, numerous toxicological studies with laboratory animals (e.g., mice, rats, mallard ducks, etc.), as well as field observational studies following marine oil spills, provide information on the effects of oil to birds and mammals. This information is at least partially transferrable to, and relevant in, the freshwater context. Most laboratory studies have focused on unweathered oils and petroleum products. Most field studies have focused on acute effects of spilled product in the early phases following a spill. Prior reviews discussing the exposure of birds and mammals to oil spills and the resultant effects include: Szaro (1977), Leighton (1982), Shales *et al.* (1989), and Hartung (1995).

Wildlife, especially birds and shoreline mammals, are typically among the most visibly affected organisms in any oil spill. Where dense populations exist, and spill coverage is extensive, the number of animals killed in the immediate aftermath of a spill can be quite large. Large numbers of geese, ducks, herons, and muskrats were reported killed following an oil spill on the St. Lawrence River (Palm, 1979; Alexander *et al.*, 1981). Numerous ducks and geese, likewise, were killed following a spill into the Monongahela River (Lemonik, 1988).

Many aquatic and semi-aquatic birds and mammals may be capable of avoiding oil-impacted areas. Where alternative unimpacted sites are available to serve the feeding and other habitat needs of these animals, as will often be the case with localized spills into freshwater systems (in contrast to large scale spills into marine systems), wildlife mortalities may be limited. Still, reports are conflicting regarding the tendency of different species to be attracted to, indifferent to, or repelled by, spilled oil products (Flickinger, 1981; Davis *et al.*, 1988; Stubblefield *et al.*, 1995).

Oil spill effects on wildlife can easily be differentiated into physical (mechanical) and toxicological (chemical) effects, the former predominating in the early phases following a spill, and the latter predominating once the spilled product has begun to weather and dissipate. Physical effects early in the spill result from the actual coating of animals with spilled product, causing severe reductions in the thermal insulative capacity and buoyancy of plumage (feathers) and pelage (fur). After early weathering processes have occurred, the oil is much more viscous and the potential for physical coating, and subsequent effects, is dramatically reduced, leaving toxicologic consequences as the greater concern. Toxicological effects generally result from the ingestion of oil and oiled food items by individuals surviving the initial spill (Hartung, 1995; Stubblefield *et al.*, 1995). This discussion will review the two types of effects separately.

Physical Effects of Oil on Wildlife. According to Hartung (1995), "essentially all of the effects of oil on biota during the acute high dose exposure stage [i.e., immediately following an oil spill] can be related to the physical properties of oils and their physical interactions with living systems." Floating oils and, to a lesser extent, beached oils, represent the predominant stressors to aquatic birds and mammals shortly after a spill has occurred. The extent of spill-induced wildlife losses will vary with the size of the spill, the location and season of the spill, the life histories and habitat requirements of species that might be exposed, the dynamics of the aquatic system into which the spill occurs, and, obviously, the type of product spilled. Animals that spend time at the water surface, such as waterfowl, muskrats, and beaver, will be at the greatest risk in any oil spill. Shoreline animals, such as small mammals and wading birds, will be less at risk.

The classic physical effect scenario for lower viscosity oils is as follows: An aquatic or semi-aquatic animal surfaces from underneath an oil slick; its plumage or pelage becomes coated with oil; this coating destroys the buoyancy and insulative capacity of the plumage or pelage; and the animal either drowns, becomes hypothermic, or seeks refuge on land (Hartung, 1995; Hartung, 1967; Davis *et al.*; 1988; Wragg, 1954; Aldrich, 1938). Starvation is often an indirect cause of death among animals not killed by hypothermia or drowning. The extent to which immediate effects of oil on exposed animals will be manifested depends on the degree to which they rely on the buoyancy and thermal insulation of their feathers or fur. All aquatic birds are heavily reliant as such; river otters, beavers, and muskrats are likewise reliant.

Oil-coated animals that seek refuge on land will be severely disadvantaged and susceptible to mortality. They will tend to experience excessive heat loss and compensatorily elevated metabolic rates (Hartung, 1967; McEwan and Koelnick, 1973; Davis *et al.*, 1988). They have been reported to exhibit abnormal behavior patterns such as excessive preening (Hunt, 1957) and loss of shyness (Davis *et al.,* 1988). Moreover, they may be poorly adapted to foraging on land. Thus, at a time when their energy demands are maximized due to elevated metabolism, their ability to feed may be severely diminished or eliminated.

Data on effects to mammals and waterfowl from spills are predominantly for marine species. At a minimum, it would be beneficial to confirm that extrapolation of marine findings to freshwater species can be confirmed with data on selected freshwater species.

Physical effects of oil can be expected to be much more severe in non-flowing, contained systems during winter months and in colder climates, and in areas where aquatic-dependent animals such as waterfowl are especially abundant. As spilled product begins to dissipate or be flushed by river/stream action from an area, and as the oil naturally weathers, physical effects will become less severe. Surviving animals then may be exposed to oil through other exposure routes, as next discussed.

Biological/Toxicological Effects of Oil on Wildlife. As time passes after an oil spill, and as the slick dissipates and weathers, the physical effects of oiling on wildlife become less prominent. At this point, oil remaining in the environment may cause adverse biological effects on birds and mammals via other routes of exposure. These routes include ingestion, inhalation, and dermal absorption. Of these three, ingestion appears to be the most significant (Stubblefield *et al.*, 1995; Hartung, 1995). Ingestion of oil may occur when animals consume oil-contaminated food, drink oil-contaminated water, or orally remove oil from plumage and pelage (preening and grooming). Studies have documented the possibility of oil-induced effects on birds' eggs when oil is transferred from the feathers of nesting birds to egg shells (Stubblefield *et al.*, 1995;

Oakley, 1990; Sharp, 1990). Hartung (1995) reviewed and summarized the mechanisms of uptake of oil by birds and mammals as well the effects on such target organs and systems as the gastro-intestinal tract, skin and eyes, respiratory system, nervous system, liver, kidneys, blood, endocrine system, reproductive system, and immune system.

Animals potentially can be affected by inhaling volatile hydrocarbons evolving from an oil spill. However, such effects would likely occur only during the initial phases of the spill when the lightest and most volatile fractions are evaporating. According to Hartung (1995), "the inhalation route of exposure is bound to fade to insignificance as the oils weather and the volatile fractions diminish greatly." When potentially toxic hydrocarbon constituents are volatilizing, the physical effects of oiling typically predominate. They will tend to overshadow any respiratory impacts or lethality due to inhalation of hydrocarbons. Reported studies suggest that hydrocarbon inhalation will not play a significant role in causing post-spill impacts to birds and mammals. Environmental conditions during and after a spill will tend to limit airborne hydrocarbon exposure levels to less than toxic concentrations (Eley *et al.*, 1989; Hartung, 1995).

Dermal absorption of hydrocarbons tends to be a relatively unimportant mechanism of toxicity to spill-impacted birds and mammals. Absorption through the skin is quite slow relative to that through the intestines and lungs (Magee, 1991). High molecular weight non-polar petroleum compounds, such as those that predominate in weathered oil, are not effectively absorbed through the skin. Oils are not inherently irritating to the skin of wildlife, although eye irritation has been reported among seals and otters exposed to spilled oil (St. Aubin, 1990).

The severity of effects resulting from the ingestion of oil will depend strongly on the status of the oil at the time it is consumed. Toxicity studies with birds and mammals indicated that weathered North Slope crude oil has very low toxicity to animals (Stubblefield *et al.*, 1995), whereas, ingested unweathered oil and petroleum products may cause adverse effects. During the time that animals may be exposed to the unweathered fraction of an oil spill, however, physical effects due to oiling will tend to overshadow toxicological effects due to other means of exposure.

Oil ingestion occurs primarily through feeding on oil-contaminated food items and through preening/grooming of oiled feathers and fur. The preening/grooming pathway will diminish in importance as an oil slick dissipates, i.e., as less oil is present on the water surface. Hartung (1963, 1967) reported that up to 50% of oil applied to the feathers of waterfowl was ingested during preening over an 8 day period, resulting in the consumption of up to 3.5 g of oil. However, McEwan and Whitehead (1980) reported that up to 48% of the oil ingested by birds during preening was excreted in the feces, i.e., it was not absorbed across the gut into the birds' tissues. Stubblefield *et al.* (1995) concluded that the risk to waterfowl from the consumption of weathered crude oil during preening was negligible.

Similar data regarding oil consumption rates by grooming mammals are not available. Some intake of oil would be expected. Significant quantities of oil may also be ingested when birds and mammals consume plant material and invertebrates contaminated with oil and oil constituents. As oil sinks and adheres to shorelines, rooted macrophytes, and bottom substrates, the risk of ingestion by feeding birds and mammals can be expected to increase.

Acutely lethal oral doses (LD_{50}, the dose of material estimated to cause mortality in 50% of a population via any route except inhalation) of crude oils and simple fuel oils have been reported to exceed 10 mL/kg body weight for waterfowl (Hartung and Hunt, 1966). Stubblefield *et al.* (1995) reported no acute toxicity among mallard ducks and ferrets ingesting up to 5 g weathered crude oil per kg body weight. Studies by Smith *et al.* (1980) indicate that acutely toxic doses for three crude oils in mice exceeded the highest doses tested, i.e., >10 to 16 g of oil per kg body weight. The U.S. EPA has established standard evaluation criteria for agricultural-use chemicals, defining as "practically non-toxic" those chemicals with LD_{50} values of >2 g/kg body weight. According to this standard, the aforementioned studies suggest that the tested petroleum materials would be considered practically non-toxic to the species tested. Moreover, predicted rates of dietary oil ingestion by aquatic birds and mammals in the vicinity of an oil spill are well below the exposure levels tested in the reported studies (Stubblefield *et al.*, 1995). Still, some studies have reported sub-lethal effects in ducks resulting from ingestion of high doses of oil (2-24 mL/kg body weight). These include diarrhea and irritated intestinal tracts (Hartung and Hunt, 1966; Hartung, 1964). Such symptoms may accelerate starvation in oil-exposed animals already suffering from elevated metabolic demands due to the physical effects of oiling (Hartung, 1995).

Contamination of organisms' food items by pollutants may lead to reduced feeding, food avoidance, or toxicity. However, Stubblefield *et al.* (1995) reported no aversion or preference by mallards of diets containing up to 10% or 20,000 mg/kg weathered crude oil. Szaro *et al.* (1978) showed no food avoidance by birds provided with food containing up to 5% unweathered crude oil. These studies suggest that avoidance of oil-contaminated food following a spill, at least after the slick has dissipated and weathered to some degree, will not be a significant factor contributing to starvation among waterfowl, and perhaps other wildlife species. Immediately following a spill, localized disruption of feeding behavior may occur in severely oiled areas among animals not suffering from the physical effects of oiling (Sharp, 1990), but such disruptions should cease after the initial phases of the spill.

Studies investigating dietary exposure of birds and mammals to oil indicate that dietary toxicity is slight. Ingestion by mallards of diets containing up to 100,000 mg weathered crude oil per kg diet caused no treatment-related mortalities or gross signs of toxicity (Stubblefield *et al.*, 1995). No significant effects on reproduction were observed among mallards consuming up to 2,000 mg weathered crude oil per kg diet (Id.). However, among ducks fed diets containing 20,000 mg weathered oil, investigators did observe a slight reduction in eggshell thickness (Id.). Also, previous studies with unweathered crude oils tested at dietary concentrations up to 5% have reported a variety of adverse effects on reproductive parameters including reduced numbers of eggs, delays in onset of egg production, and reductions in eggshell thickness and weight (Coon and Dieter, 1981; Holmes *et al.*, 1978; Harvey *et al.*, 1982; Ainley *et al.*, 1981; Hartung, 1965).

These results indicate that the more weathered an oil is, the less toxic it will be to organisms ingesting it. Dietary toxicity will more likely occur immediately following a spill. However, wildlife toxicity due to ingestion of unweathered oils during the initial post-spill period is likely to be masked by the physical effects of oiling on exposed organisms.

Studies have evaluated the potential for toxic effects to waterfowl embryos from the transfer of oil from the breast feathers of nesting birds to eggshells. Oil applied to eggs can penetrate the shells, causing direct toxic effects on the embryos, or can block shell pores, causing suffocation. Microliter quantities of unweatherd crude oil and other petroleum products have been shown to be extremely toxic to bird embryos. For example, median lethal doses for unweathered Prudhoe Bay crude oil have been reported as 18.3 μL/egg and 4.2 μL/egg for mallards and leghorn chickens, respectively (Hoffman and Albers, 1984; Couillard and Leighton, 1990). Parnell *et al.* (1985) observed that, following a spill of No. 6 diesel oil in North Carolina, 24 of 98 brown pelican nests were contaminated during the first half of the incubation period by oil transferred from the breast feathers of adults to the eggs. The hatching success of oiled eggs was significantly less than that of uncontaminated eggs.

In contrast, Stubblefield *et al.* (1995) found that weathered crude oil caused no toxic effects to embryos when applied to mallard eggs at doses up to 92 mg/egg. Coverage of greater than 33% of eggshell surfaces with weathered crude oil had no apparent inhibitory effect on gas exchange across the shell. These results suggest that initial external oiling of eggs may cause bird mortalities, but once spilled oil has weathered, adverse effects on developing embryos should be limited.

SUMMARY

Spilled oil products can affect freshwater organisms both directly, as a result of physical and toxicological processes, and indirectly, as a result of habitat impacts, nutrient cycling disruptions, and alterations in community and trophic relationships. The magnitude of effects will tend to vary with multiple parameters, the most significant of which include the type of product spilled, the flow dynamics of the system receiving the spill, the species assemblages present, climate, and the spill-response tactics employed.

Laboratory results suggest that acute toxicity can be best understood in terms of the properties and relative concentrations of the constituent hydrocarbons present in the spilled crude or petroleum product. Experimental knowledge of the chemical composition of a product is limited for predicting how oil will behave and affect exposed organisms under spill conditions. Several clues are presented on the potential for acute toxicity: 1) it is related to the solubility of spilled oil constituents; and 2) it increases with molecular weight, alkyl substitution, or carbon ring number (with solubility limits).

Toxicity of oil constituents in the aquatic environment is related to two inversely related factors: the individual compound's potency and its water solubility. In general, hydrophobic compounds are inherently more toxic per unit compound than water-soluble compounds. Nevertheless, the toxicity of hydrophobic compounds in aquatic systems is limited since only a relatively small amount is dissolved in water. Alternatively, water-soluble compounds tend to be less toxic per unit of compound compared to hydrophobic compounds. Nevertheless, more compound is present in the water column due to increased water solubility. When oil is released into the environment, water soluble compounds are primarily responsible for observed acute toxicity due to differential solubility and potency of the individual constituents.

For these reasons, the uptake, bioaccumulation, and toxicity of hydrocarbons generally follows a pattern related to carbon number. Mono- and diaromatics will tend to show the greatest uptake into organisms, because they are lipophilic enough to partition into tissues while soluble enough to be bioavailable.

Results summarized earlier in this chapter suggest that the toxicity of an oil should be predictable from its composition and that of its WSF, especially its aromatic content. The WSFs of oils are comprised primarily of the mono- and diaromatics, and toxicities of the WSFs tend to be similar to those of the individual constituents. Although it is difficult to generalize as to toxicity patterns of oils, most investigators have concluded that toxicity is related to an oil's concentrations of polyalkylated mono- and diaromatic constituents. Because of the coordinated effects of solubility and toxicity, the higher the concentrations of these aromatics (i.e., the alkylated benzenes and napthalenes) in a particular oil sample, the more toxic it will be. For example, No. 1 fuel oil contains significantly more of these aromatics in its WSF (91%) than does crude oil (15%) and is significantly more toxic. For similar reasons, weathered oils are substantially less toxic to aquatic organisms than fresh oils, at least when expressed in terms of percent WSF. Most or all of the aromatics evaporate during weathering, leaving little of the toxic fraction of the fresh oil.

With respect to crude oils, studies comparing the relative toxicities of different oils indicate that the lighter, more volatile oils (including Norman Wells and Prudhoe Bay) are more toxic to aquatic organisms than heavier, more viscous oils (including Lago Medio). No. 2 fuel oil was shown to be more toxic than No. 6 residual oil. Gasoline, in turn, was found to be more toxic than No. 2 fuel oil and Bunker C. Such relationships represent only qualitative, generalized observations. As discussed, results may differ with changes in test methodologies, test organisms, and reporting parameters.

Oil spill effects on bacteria and other microorganisms have been extensively studied due to the interest in bacteria as mediators of oil biodegradation. Bacteria tend to be resistant to hydrocarbon exposure. Many bacterial populations have been reported to be stimulated following oil spills. However, some species may suffer toxic effects, and post-spill monitoring has revealed that spill-affected bacteria populations tend to be characterized by low species diversity and a predominance of hydrocarbon-utilizing heterotrophic species. Petroleum-induced changes in bacteria populations can have secondary effects on the nutrient dynamics of freshwater systems. When bacteria shift to spilled oil as their primary carbon source, degradation of natural plant litter may diminish. Some studies have documented resultant declines in aqueous nitrogen and phosphorous levels. Still, other studies suggest that spilled oil, especially when containing high sulfur concentrations, may stimulate nitrogen-fixing cyanobacteria. This stimulation will tend to offset the nutrient demands created by increased numbers of hydrocarbon-utilizing heterotrophs.

Algal populations are often stimulated following oil spills, although there tends to be a lag phase immediately following a spill. Prior to the volatilization of the more toxic volatile hydrocarbons, inhibition of algal growth may occur. Algae appear to be adversely affected by light-end hydrocarbons as a result of membrane destruction and photosynthesis inhibition. As has been discussed, oil may induce bacteria-related changes in the nutrient dynamics of freshwater systems. Several studies have documented diminished nitrogen and phosphorous concentrations following a spill due to the decline in bacterial recycling of plant litter. These changes would portend post-spill algal declines. Other studies suggest that the spill-induced stimulation of nitrogen-fixing cyanobacteria leads to increased availability of nitrogen and resultant algal stimulation. Algae populations may also be enhanced as a result of diminished grazing from spill-affected invertebrates.

Freshwater invertebrates represent a highly diverse group of organisms whose sensitivities to petroleum exposure vary substantially. They tend to be somewhat more sensitive than algae and equally or less sensitive than some fish species. Planktonic species tend to be more sensitive than most benthic insects, crustaceans, and molluscs. Laboratory investigations have shown sub-lethal effects of hydrocarbon exposure on freshwater invertebrates at relatively low WSF concentrations. Such effects include impaired growth and reproduction. Invertebrates do accumulate hydrocarbons, and relatively high BCFs have been reported for some hydrocarbons in some species. Most invertebrates do not possess MFO activity, although it has been observed in some groups, including the phyla Arthropoda and Annelida. Hydrocarbon metabolism was reported in the hepatopancreas and green gland of the red swamp crayfish. Oil spills can result in substantial decreases in invertebrate populations. As with other organism groups, invertebrates may suffer from toxicity, physical effects (entrapment), and community-related factors (e.g., diminished food supply). Often, post-spill invertebrate communities have low species diversity and are dominated by pollution-tolerant species.

Oil spill effects on aquatic macrophytes tend to be among the more obvious and visibly disturbing. Shoreline and floating vegetation is often seen coated with oil or experiencing die-back following a spill. Macrophytes play an ecologically important role in preventing shoreline erosion and providing important habitat to wildlife species. Consequently, remedial post-spill cutting of macrophytes and oil-induced effects on vegetation stands can have significant secondary impacts on an ecosystem. Cutting of oiled vegetation has, in some cases, been shown to be counterproductive to habitat recovery. It may lead to diminished regrowth of plant stems, increased bank erosion, and greater penetration of oil into shoreline stands. Penetration of oil into soil substrates and resultant root exposure has been shown to be more threatening to aquatic vegetation than leaf and stem exposure. Soil penetration tends to be a function of water flow dynamics, soil texture, and soil organic content. Coarser and more organically enriched soils tend to experience higher penetration and, thus, cause greater effects on rooted macrophytes. Woody vegetation and perennials have been reported to be less sensitive to spilled oil than floating annual species. Studies have shown some freshwater grass, sedge, and reed species to be relatively insensitive to oil pollution and some freshwater grasses to be more tolerant of oiling than saltwater varieties.

Substantial data are available regarding the effects of spilled oil on freshwater fish. Rainbow trout have consistently been reported as being among the most sensitive freshwater species to petroleum hydrocarbons. Fish do accumulate hydrocarbons, with BCFs varying as a function of fish species, tissue type, and petroleum product in question. Fish are capable of metabolizing and rapidly excreting assimilated hydrocarbons as a function of MFO activity. Some reports suggest that adverse effects on liver function may result from MFO induction. Petroleum exposure may directly damage gill membranes in fish, adversely affecting osmoregulation and gas exchange. Osmoregulatory impairment may be especially troublesome for anadromous fish such as salmon and steelhead. Fish mortality, irregular behavior, impaired reproduction, and impaired growth have been reported as stemming from exposure to spilled petroleum products. Documented observational effects of oil spills on freshwater fish populations have ranged from extensive mortalities to minimal impacts. Even when major fish kills have occurred, population recovery has been observed, and long-term changes in fish abundance have not been reported.

Little information is available regarding the effects of spilled oil on freshwater amphibians and reptiles. Their semi- or fully-aquatic habits and high degree of surface contact render them especially vulnerable to oil exposure. Frog larvae have been reported as being more sensitive to oil than some warm water fish species. Post-spill, freshwater, observational studies have reported large numbers of dead or stressed reptiles and amphibians, even in the absence of observed dead fish and invertebrates.

Oil-impacted birds and mammals tend to receive the greatest attention from the news media following a spill. Observational studies have reported extensive post-spill mortalities of freshwater animals. Initial adverse effects tend to result from physical coating by oil. This coating disrupts the natural buoyancy and thermal insulation of fur and feathers, often leading to drowning or thermal stress. Some aquatic animals may seek refuge on land, where they may be especially vulnerable to predation or starvation. Animals that naturally spend much of their time at the water surface, especially in non-flowing systems, will be at the greatest risk.

With the gradual dissipation of a spill, physical effects become less pronounced, and toxic exposure to birds and mammals may occur. In general, ingestion of spilled oil has been reported as the primary route of toxic exposure. Inhalation and dermal absorption have been shown to be relatively insignificant means of exposure. Studies have reported relatively low toxicities of weathered oils to birds and mammals. Spilled oil may be toxic initially; but, during the phase of the spill when exposure to toxic unweathered oil occurs, adverse physical impacts on exposed animals will tend to predominate. During later phases, the physical effects diminish, simultaneously, with the weathering of the oil. Thus, following the phase of severe physical effects, oil exposure may continue, yet pose a reduced threat to birds and mammals. Laboratory toxicity studies with weathered oil have reported quite high oral thresholds and minimal avoidance of oil-contaminated food. Unweathered oil transferred to bird eggs has been shown to be highly toxic to developing embryos; however, weathered oil has been shown to be substantially less toxic. Thus, initial attempts to minimize physical contact of birds and mammals with surface oil may effectively reduce bird and mammal mortalities. Remnant oil, once weathered, should pose only a minimal toxicological threat to these animals.

The role of sediments as a sink for spilled oil and the possibility of slow releases of trapped, free product or weathered oil from sediments is acknowledged. Little field data are available on these topics regarding their contribution to environmental effects. However, studies of weathered oil can be useful in predicting such effects from sediments.

Section 5

SUMMARY AND RESEARCH NEEDS

The chemistry of a crude oil or petroleum product will generally be the principal determinant of its fate and effect(s) in the environment. Each oil is a complex mixture of hundreds of organic (and a few inorganic) compounds which differ in their solubility, toxicity, persistence, and other properties that profoundly affect their fate in, and impact on, the environment. Most oils are about 95% carbon and hydrogen, with small amounts of sulfur, nitrogen, and oxygen, and traces of other elements.

The dominant processes that influence the behavior of spilled oil are: spreading and drift, emulsion and dispersion, evaporation, dissolution, sorption/sedimentation/sinking, and degradation (photo- and bio-degradation). For the most part, these processes are the same in freshwaters as in marine waters. However, the generally lower density of freshwaters, higher sediment loads, and more turbulent waters (e.g., rapids and spillways) tend to mix spilled oil into the water column. Consequently, the likelihood of sinking oil increases.

Every oil spill will have unique characteristics that may complicate implementation of a response strategy in ways not encountered in prior spills. Factors which influence the fate and effects of spilled oil in freshwater environments include: water currents, shoreline complexity, nutrient concentrations, sediment load, water temperature, past exposure, and season.

Interpreting information from field studies of spills of opportunity can be difficult; however, findings from field studies are useful to identify dominant routes of exposure and relative degree of impact from a spill and the response. Immediately following an oil spill, effects on aquatic organisms tend to be due to physical coating or entrapment of organisms (e.g., loss of insulation and buoyancy, smothering, and disrupted swimming and feeding behaviors). Acute toxicity may occur as a result of the dissolution of oil constituents in water, and numerous laboratory studies have described the responses to oil exposure (e.g., membrane damage, systemic toxicity). However, post-spill field observations suggest that the toxic effects of spilled oil tend to be less extensive than the physical ones. The extent of direct physical contact of organisms to undissolved product seems to be the primary determinant of biological effects. The greater the probability that a plant or animal will directly encounter spilled product, before the oil has had a chance to weather or dissipate, the greater the chance that organism will be adversely affected by the spill.

The toxicity of petroleum hydrocarbon components to aquatic organisms tends to increase, at least within a class of compounds, with increasing molecular weight, alkyl substitution, or carbon ring number. Solubility follows a similar trend, and researchers have suggested that patterns in toxicity are likely due to the increased potential for uptake and absorption of the heavier or more highly substituted compounds within a class.

With improved knowledge on freshwater environmental effects, spill response strategies can be more effectively designed and implemented to protect desired habitats and/or organisms. Spill response planners can identify the types of oils, and their dominant soluble constituents, which are likely to be spilled in their areas of responsibility. With the information on freshwater spill environmental effects, planners can identify likely routes of exposure and whether sensitive wildlife may be exposed. In general, based on review of field information, those response strategies which lessen direct contact with undissolved spilled oil will reduce potential environmental impacts.

Certain research needs were identified during preparation of this review. Some were recognized in the literature sources themselves; some were merely apparent from gaps in the information available. Satisfying these research needs would go far towards improving inland spill responses, similar to the way that marine spill actions have benefited from an extensive research focus.

Authors of several of the literature reviews and technical articles accessed during the preparation of this document commented on the general scarcity of information specific to oil spills into freshwater inland systems. Although marine spills and marine organisms have received extensive attention from the scientific community, the same cannot be said of the freshwater environment. Inland oil spills tend not to be as dramatic or as catastrophic as marine spills. However, they occur with equal or greater frequency, and they have the potential to cause environmental injury, in aggregate, to an equivalent extent. Considering the extremely close and widespread association between humans and freshwater ecosystems, increased investigation into the fate and effects of oil spilled into inland waters would seem to be warranted.

Specific research areas requiring further attention include the following:

Water Soluble Fraction Testing and Method Standardization

Increased investigation of the quantitative relationships among different oils' chemical composition, WSF composition, and WSF toxicity would be highly valuable. Available research data suggest that the toxicity of an oil can be fairly accurately predicted from its chemical composition, especially its water-soluble fraction. Further investigation of WSF chemistry would seem to provide the greatest opportunity for facilitating predictions of spilled petroleum product toxicity in freshwater systems.

More data are needed to enable researchers and oil spill responders to better predict how a given petroleum product will dissolve in water, what dissolved constituents account for the product's toxicity, and how long the dissolved fraction will remain potentially toxic after a spill occurs. Thus, increased research into the chemistry and fate dynamics of WSFs is warranted. Individual chemical constituent concentrations must be measured in test exposure solutions (measurement of total petroleum hydrocarbons is not adequate), and concentration dynamics should be monitored over time. Constituent concentrations should likewise be monitored in ambient surface waters following a spill so that laboratory and field parameters may be compared.

Increased standardization of oil toxicity testing procedures is required if testing data are to be truly useful as the basis for effective spill-response decisions. Currently, laboratory toxicity results for various petroleum products are derived from studies conducted using different exposure regimes, analytical procedures, and reporting methods. Tests are conducted at different temperatures; some tests are conducted as static tests and others as continuous delivery flow-through tests; some exposures use WSFs and others use oil-in-water dispersions; some tests expose organisms to multiple dilutions of a single WSF, and others to a series of solutions bearing increasing loading rates of oil to water. It thus becomes highly speculative to compare relative toxicities of different products and relative sensitivities of different test organisms, based on the available data. Standardized testing procedures, and procedures intended to compare the toxicity of products when tested under the multiple prevailing test methods, would improve the ability of spill responders to formulate risk- and toxicity-based spill response decisions.

Weathered Oils

Marine toxicity research following the *Exxon Valdez* spill suggests that inadequate attention has been paid to testing weathered oils as opposed to fresh products. Many oils weather rapidly under field conditions, and toxicity can diminish shortly after a spill. Toxicity data based solely on responses to fresh crude oil or refined products may not be relevant in the field context for predicting organism effects past the first few days of a spill. The effects on toxicity of varying degrees of weathering, and the dynamics of the weathering process itself should be further investigated. Processes affecting the fate of spilled products should be accounted for in laboratory effects testing. Resultant information would facilitate more appropriate timing in the implementation of effective spill response strategies.

Photo-induction of PAHs has been shown to increase the toxicity of some petroleum products. Increased investigation into the toxicity-enhancing effects of PAH photo-induction is required. If photo-induced oil degradation products from a given oil are substantially more toxic than the parent product, and if a spill occurs into an area subject to intense solar radiation, spill response decisions may need to be modified accordingly.

Oil in Sediments

Sufficient information is currently lacking regarding the long-term fate and effects of oil in freshwater sediments. Weathered product may sink and persist for significant lengths of time in porous sediments or in low energy habitats. Sediment cavities may protect spilled product from weathering processes, resulting in the preservation of pockets of relatively fresh oil. Greater study is required to determine the potential effects of sediment-trapped oil on benthic community structure, nutrient dynamics, and food-chain processes. Such information is needed for making appropriate decisions regarding the extent of cleanup necessary for freshwater, oil-impacted sediments.

Vegetation Sensitivity to Oiling and Cutting Resiliency

Few studies have been conducted investigating the relative sensitivities of freshwater plants to oil and the resiliency of these plants to post-spill cutting. Information is needed to determine which plants are better able to withstand direct exposure to oil, which are more likely to regrow in the event of cutting, and which are appropriate candidates for revegetation of oil-exposed habitats. Such information would be highly useful to spill responders in deciding whether or not to cut vegetation stands exposed, or potentially exposed, to spilled oil.

Amphibians, Reptiles, and Mammals

Many inland water habitats are heavily populated with freshwater amphibians, reptiles, and mammals. Yet relatively little is known about the toxicological and physical effects of oil exposure on these animals. Most studies have concentrated on fish and invertebrates. Additional research is required to determine the relative sensitivities of these other organisms to oil. If laboratory tests are impracticable, there should at least be greater attention paid to documenting oil-related effects on amphibians, reptiles, and mammals during post-spill observational investigations.

Finally, increased monitoring and documentation of the effectiveness of inland freshwater oil spill responses are needed. In contrast to the high profile, larger-scale marine oil spills, inland spills often involve small quantities of oil spilled into relatively remote systems. Responses typically go undocumented or unpublished. Ecological monitoring often does not occur. Truly effective spill response can only be achieved through learning from past successes and failures. Determining what procedures work best for which products under which conditions is often a matter of trial and error. Information obtained during past spill responses is crucial to the formulation of effective future spill response decisions.

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Appendix A

OIL SPILL RESPONSE OPTIONS - LESSONS FROM PAST PRACTICES

Through case histories, this appendix attempts to provide practical guidance for coordinating freshwater spill response actions. It does not offer step-by-step instructions on how to select and implement the proper response for a given type of spill. Rather, a table of case histories should assist spill responders in making informed decisions. In reviewing this table, one should bear in mind the following statement quoted from Captain Robert E. Luchun's discussion of strategies and tactics for responding to open river oil spills:

> No two spills are alike. Each has its own factors that limit the ability to employ tactics that have worked in the past . . . . [I]t will be rapidly discovered that pollution response strategy must be designed within the confines of the controlling factors and conditions where the response operations will take place. The presence of natural and man-made resources at risk, environmental factors, and the availability of cleanup resources will dictate necessary strategies. (Luchun, 1992).

Table A-1. Case histories of spill responses.

RESPONSE TECHNIQUE Spill	Description of Response	Source
THE NO CLEANUP RESPONSE OPTION		
Arkansas River, Arkansas	In this 1982 oil spill, deflection booms were deployed and high pressure hot water cleaning was used, but only 42,000 of 336,000 gallons of Bunker C were recovered. No mortalities were noted and minimal wildlife oiling was reported. High runoff at the time of the spill severely frustrated oil recovery. However, runoff was also credited with rapid dilution of the spill and with limiting wildlife exposure and impacts.	Forrest *et al.*, 1985
Wolf Lodge Creek, Idaho	In this spill of gasoline into a small stream, spilled product soaked into stream-side vegetation and soils. Containment booms, sorbent materials, and pumps were used to recover spilled product from open water, but these procedures were not effective for cleaning pockets of oil trapped along shorelines. State and federal officials agreed that disturbing these areas to remove product would do more harm than good to the creek. Instead, they relied on evaporation of the spilled product to remediate the contaminated shoreline habitat.	Graves, 1985

BOOMING, ABSORBING AND PUMPING

Durbin Creek, South Carolina	In 1991, 546,000 gallons of No. 2 fuel oil spilled into this small creek. Response actions achieved greater than 95% recovery of the spilled product, a figure well above the average for a major discharge of oil. Responders used weirs, skimmers, and vacuum trucks to collect nearly one million gallons of oil/water mixture over a 5 day period. Success of the response was attributed to containment within 12 hours and placement of containment apparatus in advance of the leading edge of the oil plume.	Smith, 1993
Little Panoche Creek, California	In this 1983 crude oil spill, easy streamside access, favorable topography that concentrated contained oil, warm temperatures, and low stream flow combined to make spill recovery highly efficient. These conditions allowed for 99% recovery of the 1.3 million gallons of spilled heavy crude oil. There was sufficient heavy equipment access all along the creek. There also was a natural ravine along the creek into which oil was diverted for collection. Warm temperatures maintained the oil at an optimal viscosity for recovery. Creek flow was slow enough to continue to move the oil toward impoundment areas, yet not impair recovery. Booms were used to keep oil in the creek channel and out of side pooling areas.	Pimentell, 1985
Monongahela River, Pennsylvania	In 1988, 750,000 gallons of No. 2 diesel fuel spilled into the Monongahela River in Pittsburgh. An abundance of log and vegetation debris made surface cleanup operations difficult. A combination of factors meant that only 30% of the spilled oil could be recovered.	Clark *et al.*, 1990
Gatun Lake, Panama Canal Panama	In 1980, 168,000 gallons of Alaskan North Slope crude oil were spilled into the lake. Dense Hydrilla and tree stumps hindered booming and recovery operations. Approximately 57,000 gallons of oil were recovered using manual and mechanical methods.	Chong *et al.*, 1983
Delaware River, Delaware	In 1989, 300,000 gallons of No. 6 fuel oil spilled into the river. River temperatures were lower than the pour point of the spilled No.6 oil. As a result much of the oil formed submerged globs that were not amenable to surface recovery.	Wiltshire and Corcoran, 1991

BOOMING, ABSORBING AND PUMPING		
Roaring Run and Howell's Run, Pennsylvania	In this 1982 spill of 1,310 barrels of aviation kerosene, creek bottom sediments from pools near the primary boom recovery sites contained elevated hydrocarbon concentrations 14 months after the spill.	Guiney *et al.*, 1987a,b
Plum Creek, Virginia	In this 1973 spill of 13,000 litres of No. 2 diesel fuel, localized areas of elevated sediment hydrocarbon concentrations and adverse effects on stream benthos were detected in the vicinity of straw boom sites. In general, effects of the spill on the stream were minimal except adjacent to the booms. Investigators concluded that straw dams used to contain oil should be removed once the surface oil has been recovered to prevent the potential for long-term chronic toxicity from oil leaching from the bales into sediments and water. In this case, the straw used to trap the oil had not been adequately removed from the stream. It settled to the bottom, and then acted as an oil reservoir.	Masnik *et al.*, 1976
Oconee River, Georgia	In this diesel fuel spill into a swampy tributary of the Oconee River, spill containment was initially attempted using board booms and underflow dikes. These apparently enhanced mixing and led to the presence of downstream slicks near drinking water intakes. Subsequent placement of straw dams near the spill site, which were replaced every 6 hours, significantly improved the slick conditions.	Smith, 1973
North Platte River, Wyoming	In this spill of 359,000 gallons of crude oil from a pipeline break, river flow from an upstream reservoir was lowered after initial attempts at boom placement failed due to excessive flows. "The rapid dewatering of riffles and secondary channels resulted in high mortalities of affected infauna with significant losses among nondrought tolerant or sessile taxa, including various egg stages."	McKnight *et al.*, 1981

CHEMICAL DISPERSANTS		
Fen Lakes, Canada	In this experimental spill of 800 gallons of unweathered Norman Wells crude in shallow Fen Lakes in Alberta, Canada, densely vegetated oiled shoreline was sprayed with dispersant Corexit 9550. Researchers found that untreated oil caused more damage than dispersed oil to floating and shoreline plants. They suggested that chemical dispersion could be a useful response strategy when wildlife or wildlife habitats are at risk of exposure to beached oil.	Brown *et al.*, 1990
Fen Lakes, Canada	In other studies following an experimental crude oil spill into fen lakes in Alberta, researchers reported rapid disappearance of oil from a chemical-dispersant-treated lake. By contrast, oil remained visible in a non-treated lake for one month following the spill. No adverse ecological effects were detected in lakes treated with dispersant.	Esso, 1986
IN SITU BURNING		
Parry Sound, Lake Huron	In this 1976 spill of diesel fuel and gasoline, ice forming after the spill was found to contain up to 60% fuel. Burning was found to be the most effective cleanup method, since other recovery methods were severely hindered by the ice.	Beckett, 1979
Martinshaven, Wales	In this 1984 spill of naphtha feedstock (gasoline precursor) into a reed bed, a fire was started accidentally. The reed bed was covered with dead shoots from the previous year, and these were burned in the fire. Good regrowth was reported during the subsequent spring. Investigators speculated that without the burn, more penetration of product into rooting tissues would have occurred, causing more severe effects on the vegetation than the mere loss of dead shoots.	Baker *et al.*, 1989
BIOREMEDIATION		
Barrow, Alaska	In this 1976 spill of 55,000 gallons of gasoline into a tundra pond, fertilizer application resulted in a moderate decrease of hydrocarbon concentrations in the pond sediments. High numbers of hydrocarbon-utilizing microorganisms were found in the sediments.	Horowitz *et al.*, 1978

VEGETATION CUTTING

River Humber, United Kingdom	In this 1983 spill of 1.6 million gallons of Nigerian crude oil, Phragmites stands were heavily oiled. Experimental cutting of reeds was conducted one month after the spill. Uncut but oiled reeds experienced no apparent adverse effects in terms of growth during the subsequent spring. In contrast, cut reeds experienced diminished regrowth.	Baker *et al.*, 1989
Cape Fear River, North Carolina	In this spill of heavy fuel oil, oiled marsh vegetation was cut and removed, leaving behind immature and still-submerged plants. After 1 year, oiled/cut areas were slower to recover than oiled/uncut areas and showed evidence of increased bank erosion. Investigators suggested that remaining small plants grew after cutting but died for lack of physical support from surrounding larger vegetation. They recommended against the removal of oiled vegetation in riverine and lacustrine systems such as marsh habitats.	Baca *et al.*, 1983, 1985
Small river	In this spill of 10,000 gallons of No. 6 fuel oil into a small river with low flow velocities, mud flats and shoreline marshes were cleaned by manual cutting of oiled reeds, manual removal of oiled vegetation, and high and low pressure washing of marsh surfaces. Response activities destroyed root systems, displaced sediment substrates, and destabilized river shorelines. Investigators concluded, that cleanup activities caused more habitat damage than the spill itself. They also concluded that vegetation removal was unnecessary since little or no significant environmental damage would have occurred after initial operations had removed the bulk of the oil spilled.	Owens and Foget, 1982

VEGETATION CUTTING		
Saint Lawrence River, New York	In this 1976 spill of 307,000 gallons of No. 6 fuel oil, shoreline cattails were cut after oil penetrated 5 meters into the stands. Vegetation was cut below the oil surface level and removed by hand, leaving stalks cut below the water surface. The water level subsequently dropped, exposing the cut stalks to air. Regrowth the following spring in oiled/cut areas exceeded growth in unoiled/uncut areas, although there was much less flowering until two years after the spill. Investigators were unclear whether cutting, or the nutrients provided by the spilled oil, or both, led to the stimulated growth of the cattails.	Alexander *et al.*, 1981
SEDIMENT RAKING		
Wolf Creek, Idaho	In this 1983 spill of 25,000 gallons of gasoline, creek sediments (gravel) were mechanically raked using a bulldozer to release trapped hydrocarbons. Released gasoline was recovered using sorbent blankets, a sorbent boom, and a containment boom. Investigators found that immediately after raking, fewer benthic invertebrates and less algal activity were present in raked than unraked oiled sediments, presumably due to displacement. However, within 1 to 18 months, community compositions were similar between raked and unraked sediments. The raking was effective in eliminating sedimenttrapped product. Investigators concluded that although raking caused initial disturbance to the benthic community, it did serve to eliminate potential chronic effects due to long-term exposure to the gasoline.	Pontasch and Brusven, 1989

SEDIMENT OR BANK SOIL REMOVAL		
Little Panoche Creek, California	After 99% recovery of 31,000 barrels of spilled crude oil, USEPA made the decision to require complete removal of contaminated soil and vegetation along the creek banks. Natural weathering and biodegradation were considered unsatisfactory for clearing residual oil because: (1) impending winter conditions would not have been conducive to weathering, (2) spilled product was thick and viscous and would be persistent in the environment, and (3) the season of heavy waterfowl migration was approaching. Soil and vegetation were removed using heavy equipment. The creek contours were then restored, and additional wetland habitat (ponding areas along creek channel) was excavated. Scraped areas were replanted with two species of brush to enhance recovery. Also, the below-ground biomass of cattails remained after the scraping, providing for rapid regrowth of cattail stands.	Pimentell, 1985
ANIMAL RETRIEVAL AND CLEANING		
Ohio River, Ohio	Spill response personnel began retrieving and treating birds shortly after the spill occurred. It was estimated that only 5% of affected birds were retrieved. However, 94% of retrieved birds were successfully treated, released, and subsequently monitored in the wild.	Welte and Frank, 1991

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