

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

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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.

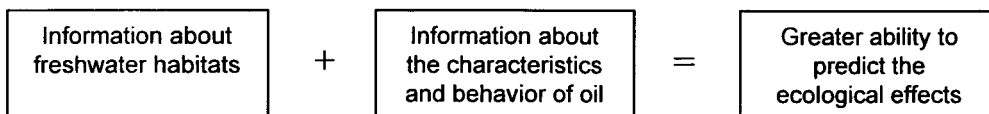
OBJECTIVES AND ORGANIZATION OF THE REVIEW

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.



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 amounts 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.

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 (C₅) and cyclohexane (C₆) 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 ($>300^\circ\text{C}$) 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 C₂₀ to C₇₀ compounds. They contain more alkanes and cycloalkanes than aromatics. Commercial 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:

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

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/s²). 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 m³ 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 m² 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, OSO₃, and SO₃H 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. Globes 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. Hrudehy 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) (Hrudehy 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 $>C_{15}$.

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 are the

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		log K _{ow}
	mg/L	μmole/L	
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 $\mu\text{g/L}$ at 5.2°C and 55.7 $\mu\text{g/L}$ 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 ‰ 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 ‰)		
	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