

Exxon Production Research Company

SPECIAL REPORT

The Fate of Petroleum in the Marine Environment

R. B. WHEELER

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SUMMARY

This report outlines progress toward understanding the fate of petroleum spilled in the marine environment. The report updates the 1975 National Academy of Sciences report "*Petroleum in the Marine Environment*"¹ and emphasizes the fate of oil in the higher latitudes. The physical, chemical, and biodegradative processes throughout the history of an oilspill are covered in this report. An attempt is made to identify processes dominating movement and weathering at various times after the spill and, when possible, to present equations for the prediction of the effects of these processes. High-priority areas for future research are outlined.

Three conclusions were reached:

1. Because of the complexity and flux of critical parameters, such as composition and environmental conditions, during slick life, no process has been successfully modeled beyond a first approximation. The most useful models are stochastic, determining the relative probability of various outcomes.
2. Nearshore high-spill risk areas should be identified to expedite cleanup in a large-scale ($>160\text{-meter}^3$) accident. Risk analyses should include spill frequency estimates based on the volume of tanker traffic and volume of offshore production, oilspill trajectory simulation, and environmental impact assessment to inshore recreational and biological resources. Contingency plans should be drafted for high-risk areas.
3. Given sufficient time, natural processes, such as evaporation, biodegradation, and sedimentation, effectively reduce the destructive potential of oilspills. Man should continue to develop techniques for enhancing and accelerating natural processes.

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INTRODUCTION

American society in the past decade has had two major energy concerns, often in diametric opposition. Increased population and consumer demands have generated an ever-increasing energy need, while ecology and environmental protection have become common, important issues.

Increased industrialization and continual development of agricultural technology, necessary to meet the needs and demands of America and the world, require more energy. In the United States, the largest energy source is fossil fuels, both domestic and foreign. With increased demand for fossil fuels and dwindling domestic reserves, new areas have been exploited, and more oil is imported from abroad than ever before. Oil retrieval from such remote places as the Outer Continental Shelves (OCS) or the Alaskan North Slope requires long-distance oil transport, either by pipeline or by tanker. Figure 1 shows the steady increase in worldwide transportation of petroleum; from 1968 to 1973 as the oil volume produced and transported in the marine environment increased, the frequency of accidental and nonaccidental releases of petroleum into marine waters also increased. However, recent technological developments and legislation work to ameliorate this problem.

In March 1967, the *S. S. Torrey Canyon* ran aground near the Scilly Isles, spilling 1.08×10^8 kilograms of Kuwait crude oil into the English Channel to wash ashore at Brittany, France, and Cornwall, England. Almost two years later Union Oil Company well 21 at platform A in the Santa Barbara Channel in California blew out, and oil flow diverted to an ocean floor fracture, making the flow nearly impossible to halt. The accident released 2.7×10^6 to 9.08×10^6 kilograms of crude oil into the channel. The results included miles of fouled shoreline, possibly thousands of dead birds, and many irate citizens.²

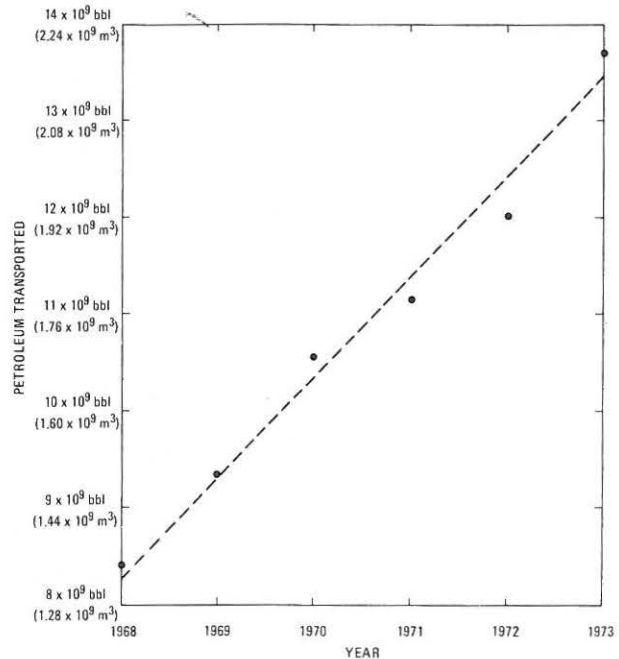


Figure 1. The worldwide marine transport of petroleum.

These major accidents and other more recent episodes have increased public awareness and sensitivity toward the threat of oil in the marine environment. Many scientific studies on the fate and effects of oilspills have been published since the late 1960s. Other more sensational and less scientific literature has portrayed a subjective viewpoint.

Oilspills are not new to the United States. During the first seven months of 1942, German submarines sank 42 tankers off the eastern seaboard of the United States, releasing 4.5×10^8 kilograms of crude and refined oils into the coastal waters.³ This is roughly twice as much petroleum as the *Amoco Cadiz* spilled near Brittany in March 1978. Yet, other than the aesthetic damage to beaches, Campbell et al.³ cannot identify any significant environmental damage from those spills.

Furthermore, the relative significance of these occasional, but large and sensational, accidents must be kept in perspective. Figure 2 shows the relative magnitudes of sources of petroleum hydrocarbons entering the marine environment. The offshore oil production category, including incidents such as the Santa Barbara spill and the Ekofisk Bravo blowout in the North Sea, constitutes only 1.3 percent. Marine transportation is a much larger (34.9 percent) category. Less than 5 percent of that 34.9 percent, however, is attributable to accidental releases⁴ and even fewer oil releases ever appear in the news media. The accidental petroleum release into the marine environment amounts to less than natural seeps (9.8 percent), of which the Santa Barbara area has several.⁵

Differing significantly from most other petroleum pollution sources, accidental inputs are acute, releasing a large volume of petroleum into a small area at a high rate. Consequently, the effects of accidental inputs may be intensified relative to the type of chronic discharge from industrial and municipal sources.

The following discussion reviews the fate of oil released in the marine environment under acute or accidental conditions. This report updates the thorough National Academy of Sciences report,¹ emphasizing the fate of oil in higher latitude environments and

development of modeling techniques. A thorough understanding of the natural fate of spilled oil is critical for coping with accidental spills.

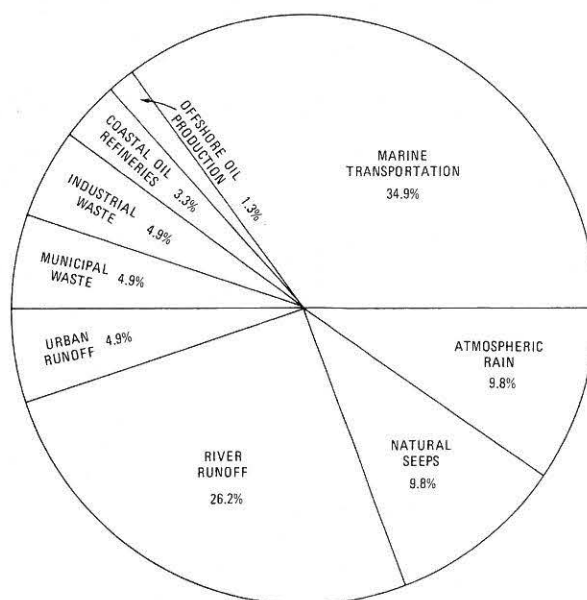


Figure 2. The budget of petroleum hydrocarbons introduced into the oceans (adapted from National Academy of Sciences¹).

SPREADING

Several processes interact to alter the distribution and composition of petroleum released into the marine environment. Spreading is the first, most significant process and is controlled by the physical and chemical properties of the oil and environmental conditions into which it is released. Figure 3 shows that spreading remains the dominant process for about 10 hours after the spill.

Although related to chemical composition and processes, spreading is a physical phenomenon. Fay⁶ defined four principal forces or processes in oil spread on a calm sea: gravitational, surface tension, inertial,

and frictional (fig. 4). The gravitational force causes lateral spreading in the direction of decreasing film thickness. This force is proportional to the film thickness, thickness gradient, and density difference between water and oil. The second force causing spreading is defined by the spreading coefficient σ , the difference between the air-water surface tension and sum of the air-oil and oil-water surface tensions. This force, independent of film thickness, becomes the dominant process in the final spreading phase (fig. 5). Fay⁷ states that spreading ends when the removal of volatile fractions reduces σ to 0.

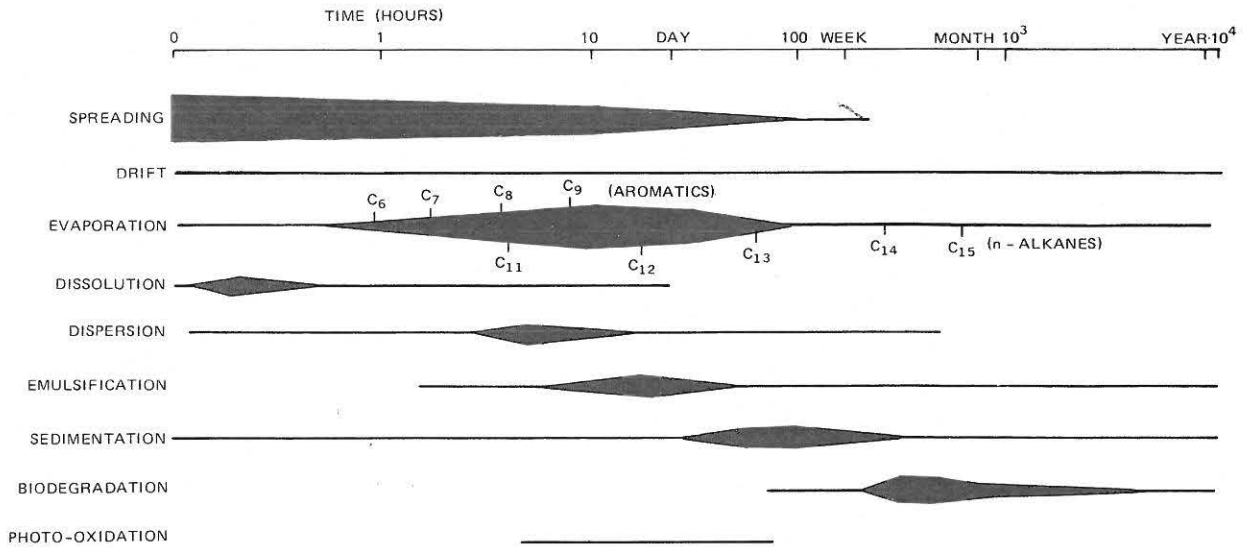


Figure 3. Processes versus time elapsed since the spill. The line length indicates the probable timespan of any process. The line width indicates the relative magnitude of the process through time and in relation to other contemporary processes.

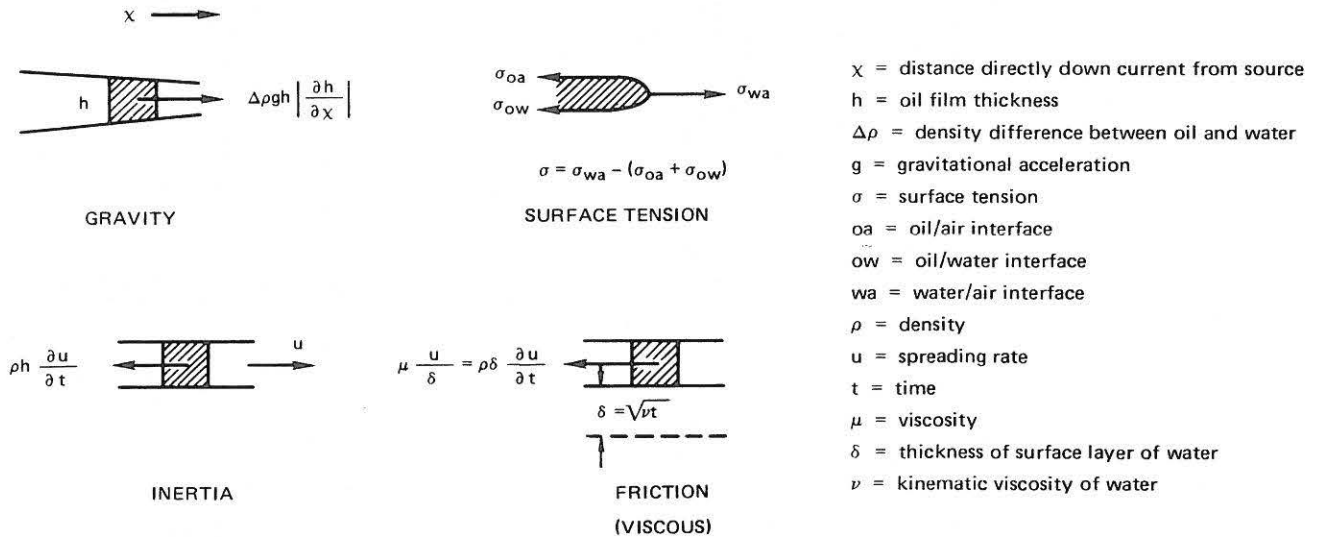


Figure 4. The four forces acting on an oil film (from Fay⁷).

Spreading forces are retarded by the inertia of the oil body and oil-water friction. Inertia, a function of the thickness, density, and acceleration of the oil slick, diminishes rapidly as spreading proceeds and dominates for only the first 10^3 to 10^4 seconds after the

spill (fig. 5). Simultaneously, friction between the slick and surface water increases the thickness of the viscous water layer beneath the slick. Viscous retardation overcomes inertial forces and remains the dominant antispreading force for the rest of the spreading process.

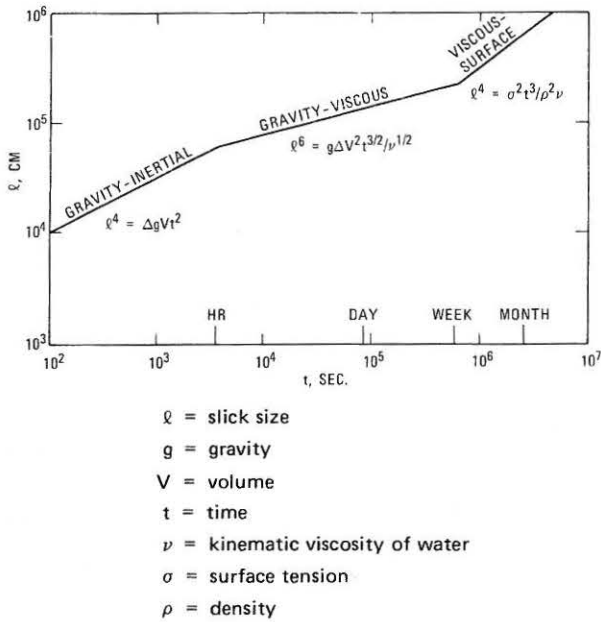


Figure 5. The size ξ of an oil slick as a function of time t for a 9.08×10^6 kilogram spill (from Fay⁶). Reproduced by permission from Plenum Press, New York, © 1969 and the author.

Obviously, changes in the physical properties and configuration of a slick alter the magnitude of the various forces. Figure 5 shows that the spreading regime between one hour and one week after the spill is dominated by gravitational spreading and frictional (viscous) retardation forces. This time interval is most critical in cleanup. Buckmaster⁸ derived this equation for slick dimensions during the gravity-viscous spreading phase:

$$R(t) = 1.76 (g\Delta)^{1/4} V^{1/2} \nu^{-1/8} t^{3/8} \quad *$$

where $2R(t)$ is the width of the slick at time t ; Δ , fractional density difference between oil and water; V , volume of oil; ν , kinematic viscosity of water; and g , gravitational acceleration.

The mathematical model holds only for spreading on calm seas, the exceptional case. Stolzenback et al.⁹ state that spreading comes from short-period ($< 10^3$ -second), small-scale ($< 10^3$ -meter) atmospheric fluctuations. In turbulent water characteristic of the open sea, wind and wave action dominates the distortion and distribution of the spreading slick. For example, slicks rapidly become elongate parallel to the prevailing wind direction; the major and minor dimensions continue to diverge (fig. 6).

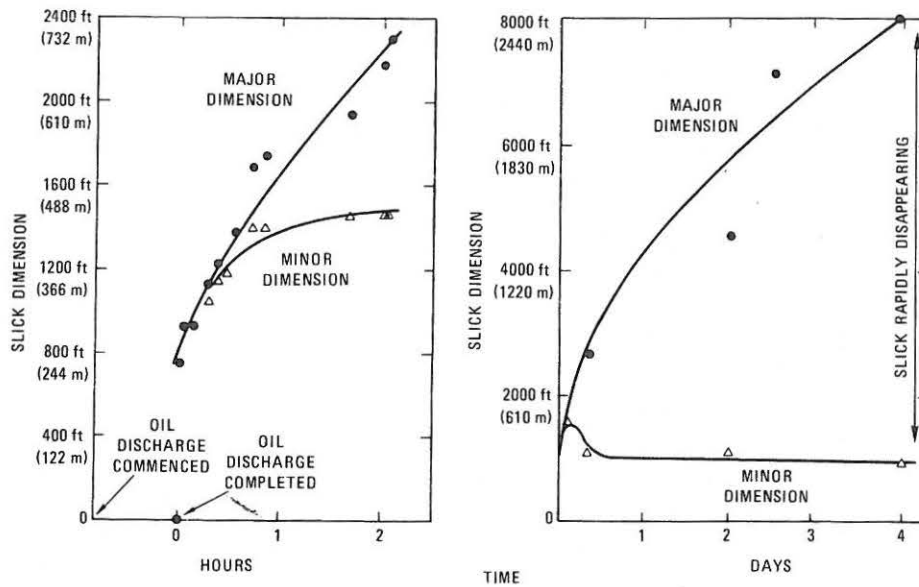


Figure 6. The relation of slick development with time (from Jeffery¹⁰).

Murray¹¹ proposed the application of turbulent diffusion theories for the prediction of spreading. Diffusion is the mass transfer of spilled oil by random eddy motion. This process is analogous to molecular diffusion although more complex because of the range of vortex sizes.

Taylor diffusion theory predicts the rate of slick expansion and shape based on the standard deviation of particle distances from the source. For short diffusion times $\sigma_y \propto x^{1/2}$, where x is the distance directly down current from the source and σ_y , standard deviation of particle diffusion measured normal to x . Figure 7 relates the observed expansion of several oil slicks to calculated dimensions for the turbulent diffusion and surface tension theories. The Taylor diffusion theory more accurately represents slick behavior under normal marine conditions.

However, the Taylor theory cannot be used to predict oil concentration or thickness. Fickian diffusion theory permits calculation of the diffusion rate as a function of the rate of concentration change with respect to time and distance downstream. Furthermore, the concentration at the apparent boundary, for example, as observed from the air can be calculated from:

$$W = \frac{2Q}{(2\pi e)^{1/2} UC_b} \quad *$$

where C_b is the boundary concentration; W , slick width; U , current velocity; Q , oil emission rate; and e , natural constant. The maximum extent of the apparent boundary concentration contour is

$$L = Q^2 / (4 \pi KUC_b^2) \quad *$$

The ratio λ of slick width to length is

$$\lambda = \frac{4(2\pi)^{1/2} KC_b}{Qe^{1/2}} \quad *$$

where K is the diffusion coefficient and C_b , empirically determined boundary concentration.¹¹

Spreading increases slick surface area, accelerating rates of weathering and degradation. As an oil is continually altered, its spreading processes, such as spreading coefficient, are also changed. Within several hours, over 90 percent of the hydrocarbons lighter than C_{10} can be removed by evaporation or dissolution.¹² The result is a progressive decrease in slick volume and corresponding increase in viscosity and specific gravity (table 1).

Inhomogeneities in the slick result in nonuniform thickness. Monitoring experimental spills, Jeffery¹⁰ noted the formation of thick oil patches soon after the spill, persisting after the remainder of the spill had disappeared. Oil pancakes up to 15 cm thick with surface areas from 10^2 to 10^4 meters² were reported after the *Argo Merchant* spill.¹⁴ Initially, this variability may be from differential spreading rates among different components. Phillips and Groseva¹⁵ demonstrated experimentally that hydrocarbon spreading coefficients vary inversely with molecular weight (fig. 8). Other concurrent processes (evaporation, dissolution, and emulsification) contribute to the inhomogeneity. Wind alone tends to pile up oil at the downwind slick edge.¹⁶

Cold water temperatures cause oil to spread more slowly. The difference is negligible except for high-viscosity oils such as bunker C. If the oil pour point is higher than the ambient water temperature, the oil immediately forms semisolid floating lumps on contact with the water. Table 2 shows a representative list of pour points for various crude oils. The likelihood of sufficiently cold water temperatures for lump formation is slim, although pour points for residual oils may reach polar and subpolar water temperatures.

Figure 3 indicates that within ten days after a spill, the floating oil is largely devoid of volatile components lighter than C_{10} and is gradually forming emulsions. By this time, enlargement of the slick by actual spreading is subordinate to fragmentation and dispersion of the semisolid lumps.⁹ The actual time required for this process is proportional to the spilled oil volume.

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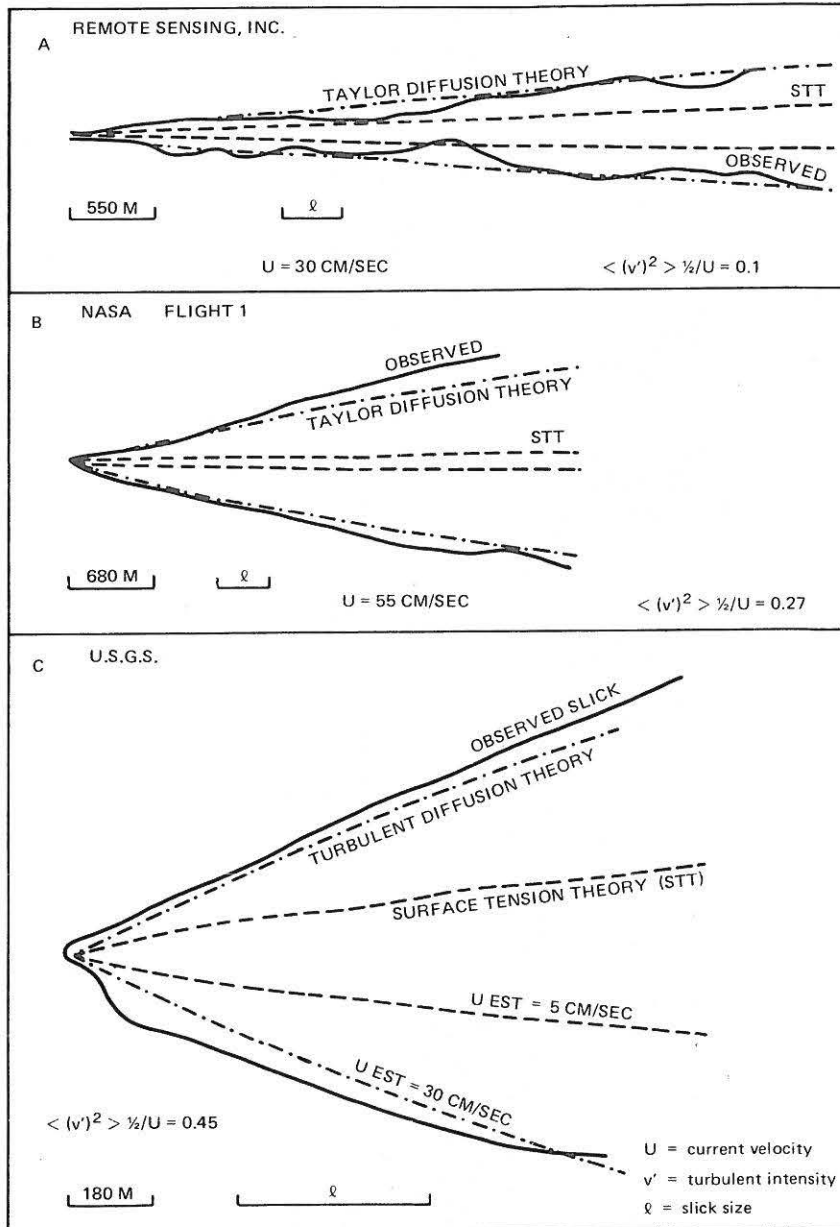


Figure 7. The comparison between observed slicks and slick outline predicted by the Taylor diffusion theory and surface tension theory of Fay.⁶ In A and B the current speed was observed onsite. In C the current speed is estimated at the average value for the incident (29 cm/second) for the turbulence theory and estimated at 5 cm/second for the surface tension theory to maximize possible agreement between Fay's theory and the observation. This figure is from Murray.¹¹ Reproduced by permission from American Society of Limnology and Oceanography, Inc., Ann Arbor, Michigan, © 1972.

Oil	Time Weathered, hours	Density, g/ml	Kinematic Viscosity, mm ² /sec*
A	0	0.862	18.78
A	8	.890	40.13
A	24	.891	47.07
A	48	.894	56.02
A	168	.903	97.53
B	0	.851	15.40
B	8	.896	28.39
B	24	.901	34.29
B	48	.908	53.88
B	168	.914	73.96

*Millimeter²/second = centistoke.

Table 1. The density and kinematic viscosity of two weathered crude oils (from Rostad¹³).

Oil	Crude, °C	Gas oil, °C*
Abu Dhabi, Murban	-12	38
Prudhoe Bay	-9	-
Arabian light	-26	32
Arabian heavy	-34	32
Iranian light	-12	35
Iranian heavy	-21	34
Tijuana light	-43	-
Kuwait	-20	-
Ekofisk	-5	-

* 343 to 565°C fraction, average carbon number C_{28.5}

Table 2. The pour points for common crude oils and selected gas oil fractions (adapted from Esso International, Inc.¹⁷).

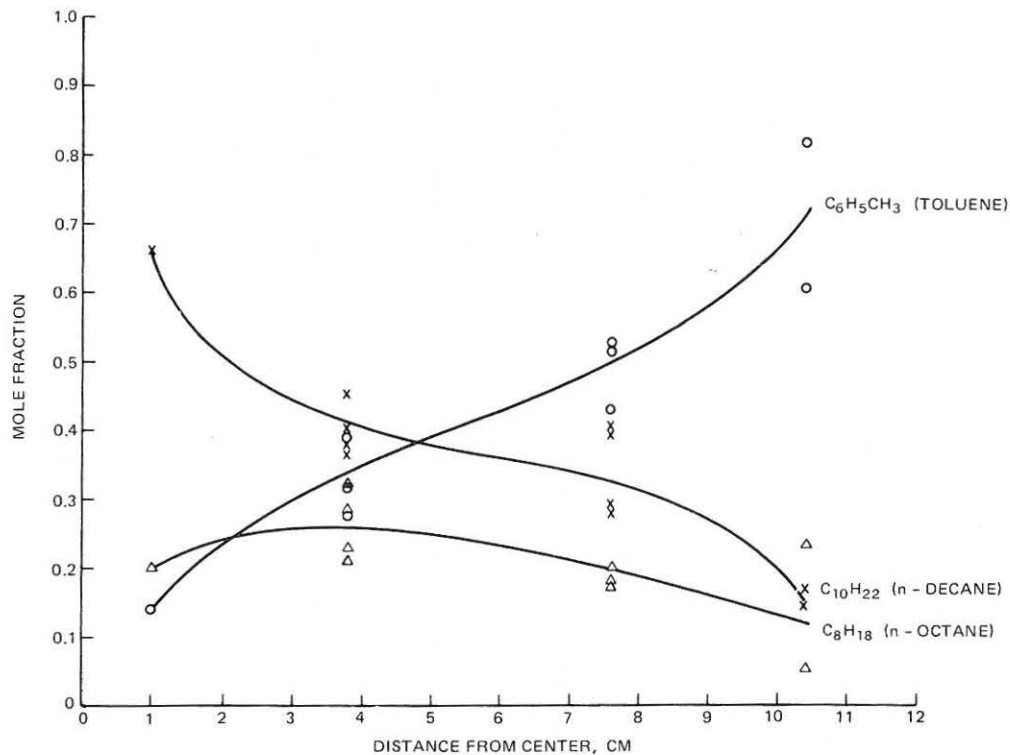


Figure 8. The mole fraction versus distance for a synthetic mixture equimolar in toluene, n-octane, and n-decane spreading on water 5 seconds after the beginning of spreading (from Phillips, et al.¹⁵). Reprinted from Separation Science and Technology, 10 (1975) by courtesy of Marcel Dekker, Inc., New York, © 1975.

With increased exploitation of high-latitude environments for petroleum production, these processes must be considered under polar conditions. Chen et al.,¹⁸ using Fay's model for spreading on a calm sea, modeled the gravity-viscous oil spread on an ice surface. Spreading rates vary according to temperature, oil type, and oil volume. The equation

$$(R/V^{1/3}) = 0.24 (t \rho g V^{1/3}/\mu)^{1/5} + C$$

where R is the slick radius; ρ , oil density; V, volume; μ , viscosity; t, time; C, a constant; and g, gravitational acceleration, seems to hold for most cases. Surface roughness of the ice is insignificant relative to the other factors.¹⁸ Table 3 shows the magnitudes of temperature-induced viscosity changes, which may be the dominant controlling factors.

Beneath the ice, the oil spread is severely inhibited. Pockets, pressure ridges, and other surface ir-

regularities, which reduce turbulence and act as natural barriers, help contain the oil. Oil under ice adheres to the lower ice surface, and small quantities migrate up through pores. Further freezing after a spill results in new ice formation below the oil. This ice traps and isolates the oil from the environment until the ice thaws.¹⁸

Elapsed time, min.	Viscosity, millipascal-second*		
	-3 °C	-8 °C	-14 °C
0	9.6	13.0	18.1
10	11.4	14.2	19.8
20	13.8	15.8	20.9
30	15.0	17.9	22.0
40	16.8	18.9	23.7
50	18.7	20.0	24.5

*Millipascal-second = centipoise.

Table 3. Viscosity (adapted from Chen, et al.¹⁸).

DRIFT

Drift, or advection, is the movement of the center of mass of an oil slick. Controlled by wind, waves, and surface currents, drift is independent of spreading and spill volume.

Modeling drift trajectories and drift rates is an integral part of planning and executing containment and cleanup. Because of increasing petroleum transportation and production in coastal waters, the United States and Canadian Governments are funding drift modeling studies for various seaboard regions of high exposure.¹⁴⁻²³ The goal is adequate model coverage in these areas to identify high-risk coastal localities and to rapidly predict spill behavior in a major accident.

Modeling slick behavior depends on the availability of abundant, accurate wind and current data and a good empirical model. The model accuracy is particularly critical in coastal regions where drifting oil must be intercepted quickly before reaching the shore. Spreading becomes increasingly important with respect to drift closer to shore, but either process may result in the small-scale movement of oil onshore.

Wind shear stress at the oil-water interface, wind-induced and nonwind-induced surface currents, and wave action are the major parameters governing movement. Nonwind-induced currents driven by tides and density differentials among water masses are usually well documented in coastal regions where their effects are most important. Another major parameter is the horizontal wind velocity, measured 10 meters above the stillwater level.

Various drift modeling techniques appear in the recent literature. Stolzenback et al.⁹ thoroughly reviewed the state of the art of modeling slick movement. The following discussion is based largely on their analysis.

WIND FIELD MODELS

Determination of the wind fields is critical to modeling slick advection. The goal of wind field modeling is to determine a single probable trajectory or distribution of possible trajectories. The latter approach is

critical in regional risk assessment. Only wind patterns on the scale of weather systems with a fluctuation period $>10^5$ seconds and a lateral extent $>10^5$ meters are pertinent to drift modeling. Smaller scale fluctuations mentioned above tend to be part of spreading mechanisms.

Wind fields vary spatially and temporally. Temporal variations decide movement of the weather system while spatial variations are related to the drift speed of the slick. Because temporal variations are greater by nearly two orders of magnitude, spatial variations are considered insignificant.

Wind fields may be modeled deterministically, using appropriate governing equations, or stochastically, using statistical derivations. Wind fields may also be modeled by interpolation and extrapolation, using actual wind measurements. Actual wind measurements, usually from land-based stations but occasionally from island stations, weather ships, or transmitting buoys, can be used directly at the time of the spill. Time series analysis of historical data allows extraction of periodic factors (for example, seasonal or diurnal), leaving only the stochastic component with a vector sum of 0. Such a model is particularly valuable for analyzing short-term transport in nearshore localities and for predicting where along a shore the slick may ground. The primary limitation of this technique is data coverage of sufficient frequency and density. The normal 1- to 3-hour interval is adequate, but the average distance between stations is more than 160 kilometers.

Along coasts data density is critical because of topographic variability and complex wind patterns developing at the convergence of marine and continental air masses. Coastal wind models accurately simulating the observed features are available but are so complex as to be prohibitively expensive for long time series.

The stochastic component of the time series based on historical sequences is simulated using the statistical parameters, usually mean, variance, and covariance, of the probability distribution. A synthetic random sequence matching these statistical

properties provides valuable information on the probability of a given drift rate and trajectory.

Synoptic pressure field models can be used to estimate wind systems above the planetary boundary layer. Surface winds are derived from this estimate by mathematical models. Synoptic pressure fields provide good temporal coverage for an area and are best with strong, persistent winds. The fields are not a good estimate of the windspeed or direction in nearshore areas. Surface wind models from synoptic pressure fields are only as accurate as the initial estimate of geostrophic flow. The largest error component is in calculation of the pressure gradient. This technique compares favorably with models based on wind measurements in offshore areas where the limiting conditions are not breached.

DRIFT MODELS

Various applications of wind and current models exist for the derivation of synthetic drift trajectories.

Stokes²⁴ developed a theory for the mass transport of particles at a water body surface by wind-driven wave action. Semirandom particle diffusion with a dominant vector in the prevailing wind direction causes advection. This process results in transport rates roughly 2 percent of the wind velocity. Neither Stokes nor any later investigators^{25,26} have accounted for the effect of a viscous surface film on processes at the water surface^{27,28} or for the drift velocity differences between the oil slick and the underlying surface water.²⁹ Alofs and Reisbig²⁷ tested the Stokes theory experimentally, eliminating the backflow phenomenon peculiar to wave tank simulations, and found experimental values deviating significantly from previously accepted Stokes predictions.

In wave advection, the wave spectrum at any time is assumed to be only a function of wind generation of waves over a specified time period. No distinction is made between the components of sea waves and swell waves. Pierson et al.³⁰ explain that surface wave spectra are composed of several wave systems with different periods and directions. The majority of these

components are swell waves, relict of a wind-generated sea at a time and locality remote to the slick. Wave advection models account only for the effect of sea waves generated and active in their original place.

Therefore, although slick advection by waves is a significant factor, the available theoretical models have serious shortcomings in predicting such movement. Furthermore, wave advection is unlikely to be the sole factor in slick movement.

Wind-induced currents are another component for modeling slick advection. The wind factor approach, based on surface shear stress of the wind, is simple and popular. The drift vector is calculated usually as 3 to 5 percent of the wind velocity. This calculation requires little computation beyond simulation of the wind field, the first step in most drift models. Teeson et al.³¹ used the wind drift factor approach but included a deflection angle in the trajectory. The deflection angle was postulated as a result of the Eckman effect, its magnitude ranging from 0 to 0.35 radian (0 to 20 degrees) as a function of latitude. In hindcasting specific spills, investigators have found different variations in magnitude which appear to fit the available data for an individual case. The lack of consistency among incidents suggests that the ability to fit the data is a contrived artifact of the hindcast approach and that other undefined factors must be involved in advection. The models have proven inaccurate for universal application.

Wind-induced surface currents appear to affect only the upper few millimeters of the water column while

surface waters containing dye dispersed through the upper 10 to 100 centimeters may move more slowly. Movement of this thicker layer is controlled by nonwind-induced current activity, such as tides and density-driven currents. Many drift models combine the wind-drift factor with some nonwind-induced current drift factor, usually 100 percent of the current vector.^{32,33} However, Schwartzberg³⁴ allowed only 56 percent of the current velocity for the current factor.

No model can account for advective forces from wind shear stress and wave action. This situation is a critical shortcoming because both effects are of the same magnitude, 2 percent of wind velocity for waves and 3 to 5 percent of wind velocity for shear stress. Furthermore, the combined effects of wind and waves are not simply additive. A portion of the surface shear stress is involved in wave generation, and wave action appears to retard wind-driven slick movement.²⁹

The wind factor approach offers the best simulation of drift trajectories when a dynamic wind field model is implemented.^{35,36} Although the best technique available, it has limited ability to predict the slick location after a spill. The technique can be used effectively, however, to predict trajectories for evaluating risk factors for shoreline impact of drifting oil.

The development of a detailed physical model integrating the various drift elements above is a difficult task. Even if available, the model would be too complex for general use. However, such a comprehensive model could supplement our understanding of the relationship of wind drift factors to water depth, wind field, and geographic location.

EVAPORATION

Evaporation and dissolution are the first two processes of degradation of oil released onto the water. These processes are concomitant, interrelated, and subject to the same environmental conditions.

Evaporation is the mass transfer of petroleum hydrocarbons from the liquid oil to the vapor phase. The composition, surface area, and physical proper-

ties of the oil; wind velocity; air and sea temperatures; sea state; and intensity of solar radiation affect hydrocarbon evaporation rates. Fallah and Stark³⁶ proposed the following equation for calculating the evaporation rate of hydrocarbons from a mixed hydrocarbon substrate:

$$dV/dt = KA^\beta [U(z)]^\alpha (P_s - P_a) \quad *$$

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where A is the liquid surface area; $U(z)$, windspeed at height z above the liquid surface; P_s , saturation vapor pressure at the liquid surface temperature; P_a , partial vapor pressure in the air upwind of the liquid surface; K , α , and β , constants; V , volume; and t , time.

The evaporation rate for a specific hydrocarbon is a function of its vapor pressure. Hydrocarbon rates in a crude oil substrate are not equivalent to evaporation rates from single-component liquids.³⁸ Vapor pressures within each hydrocarbon class, such as *n*- and isoalkanes, cycloalkanes, and aromatics, tend to increase with decreasing molecular weight (fig. 9). Isoalkanes generally have the highest vapor pressures while aromatics have the lowest. The distribution of aromatics in a crude oil is concentrated at the high-boiling end of the spectrum. Consequently, an oil slick is depleted in light, low-boiling fractions and enriched in aromatics as evaporation proceeds.

Figure 3 shows approximate times when specific hydrocarbon fractions disappear from a slick. Although the data came from two independent studies, the experimental conditions were similar; the trends shown are probably valid. Although incomplete, the data show that aromatics lag behind paraffins. The evaporation of heavier hydrocarbons ($>C_{15}$) continues for long time periods, such as 10^3 hours, but rates are insignificant after $\sim 10^2$ hours. As a rule, components with vapor pressures higher than *n*-octane do not persist, and those with vapor pressures lower than *n*-octadecane do not evaporate appreciably under normal conditions.³⁸

Changes in the physical properties of the oil (table 1) resulting from the loss of volatile hydrocarbons inhibit spreading and molecular diffusion of the remaining oil components. Fallah and Stark³⁶ improved the Pasquill equation with a random model to account for environmental factors affecting evaporation and changes in the physical properties of the oil. Wind velocity and the resulting sea state are the principal environmental factors influencing evaporation. Even under cold conditions, such as the North Sea, evaporation proceeds rapidly with a fresh wind (table 4). Sea spray and foam in a sea state ≥ 5 on the Beaufort scale increase evaporation by

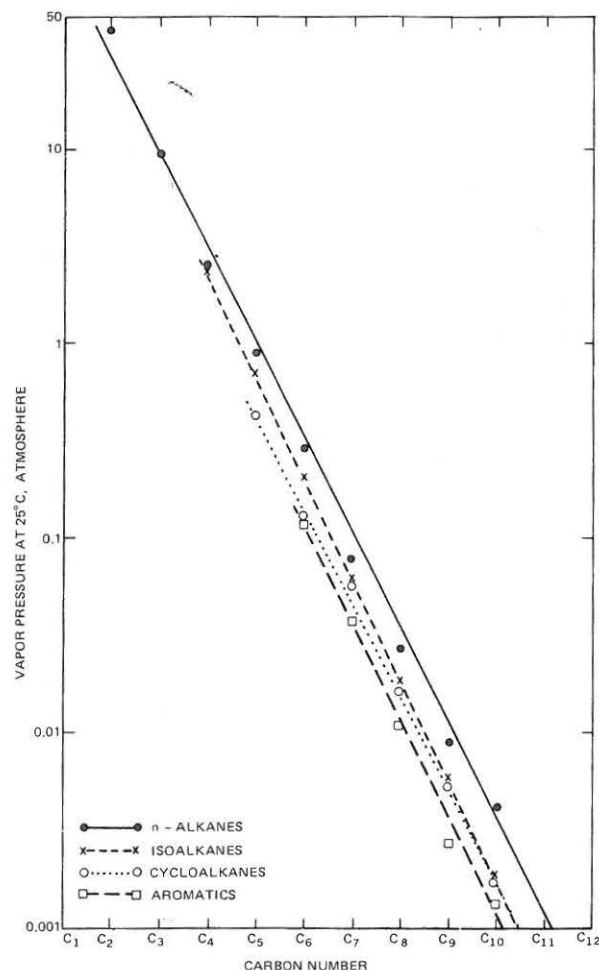


Figure 9. The vapor pressure versus carbon number for selected hydrocarbons from C_2 to C_{10} (adapted from Rossini³⁹ by permission from Thermodynamics Research Center, Texas A & M University).

substantially increasing the oil surface area exposed to the atmosphere. Spreading also increases the surface area of a slick, enhancing molecular exchange between the oil and the atmosphere.

Evaporation is the most substantial initial degradative process. Table 4 shows that 50 percent of the oilspill volume may be evaporated within the first 24 hours. Spills of refined products, such as kerosene and gasoline, may evaporate completely. Preliminary tests on the Ekofisk Bravo oil slick indicated that over

60 percent of its original components had evaporated by the ninth day.⁴⁰ Because the blowout lasted almost eight days, the actual age of the slick sample could have been from one to nine days, depending on when released. Therefore, the evaporation rate could be faster.

Evaporation rates become extremely slow by 10² hours, when the remaining oil has formed semisolid emulsions or tar lumps. However, evaporation remains the significant compositional alteration process on floating petroleum residues from 10² to 10⁴ hours.⁴¹

Sea states (Beaufort scale)	Low (2 - 3)	Medium (4 - 5)	High (6)	No dispersant action (≥ 7)
Spill volume, m ³	100	100	100	100
Evaporation loss I (first day), %	30	35	40	50
Residual oil volume A, m ³	70	65	60	50
Primary cleanup efficiency, %	70	50	30	—
Residual oil volume B, m ³	21	32.5	42	50
Evaporation loss II (5 days), %	20	15	10	—
Residual oil volume C, m ³	16.8	27.6	37.8	50
Natural dispersion — daily loss rates for 5 days only, %	10	15	25	30
Residual oil volume D before second cleanup, m ³	9.9	12.3	9.0	8.4
Secondary cleanup efficiency, %	40	30	20	—
Residual oil volume E reaching the beaches, m ³	5.9	8.6	7.2	8.4

Table 4. The estimated effects of evaporation, natural dispersion, and cleanup on the North Sea oil spill (from Rostad¹³).

DISSOLUTION

Similar to evaporation, dissolution is the mass transfer of hydrocarbons from the floating or suspended petroleum into the water column. The rate and extent of dissolution depend on oil composition and physical properties, extent of spreading, water temperature, turbulence, and amount of dispersion.

The solubilities of organic compounds decrease from the more polar compounds containing nitrogen, sulfur, and oxygen (NSO) to aromatics and alkanes (fig. 10). McAuliffe⁴² determined that branched saturated hydrocarbons of a specific carbon number have a higher solubility than straight-chain paraffins, not because of structural differences with respect to

water but because of higher vapor pressure (greater fugacity), as shown in figure 8. Among other hydrocarbon groups, solubility is a function of molar volume, inversely proportional to the degree of unsaturated bonding (acetylenes > diolefins > olefins > paraffins) and ring closure.⁴² Within any homologous series of hydrocarbons, lower molecular weight compounds are more soluble. Some hydrocarbons with lower vapor pressures and low solubilities, such as polynuclear aromatic hydrocarbons, have short half-lives in water.⁴³ In spite of low vapor pressures, these often toxic components may evaporate rapidly because of their high activity coefficients in water.

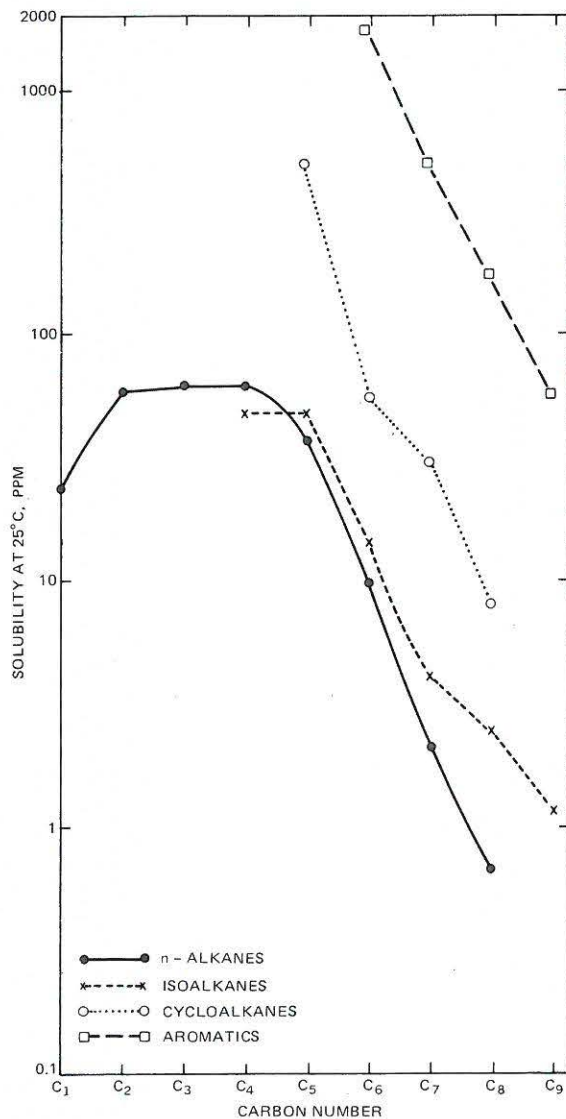


Figure 10. The solubility versus carbon number for selected hydrocarbons, C₁ to C₉ (adapted from Rossini³⁹ with permission from Thermodynamics Research Center, Texas A & M University).

Physical processes, such as spreading, turbulence, and dispersion, or oil-in-water (o/w) emulsification, favor degradative dissolution by increasing the oil surface area exposed to water. Solution and evaporation are self-limiting processes. As low-boiling liquid fractions are removed, changes in physical properties

of the oil slick, such as increased density and viscosity, inhibit spreading, turbulent diffusion of particles, and molecular diffusion of the remaining volatile components. McAuliffe¹² found wind velocity and sea state more critical than water temperature in the disappearance rate of hydrocarbons from a slick.

In a closed system with no evaporation, hydrocarbon concentrations in water under an oil slick depend on the solubility of each component and its initial mole fraction in the oil. Solubility experiments monitoring hydrocarbon concentrations in the water under oil slicks under natural conditions yield different results. Studying four experimental oil slicks, McAuliffe¹² found elevated concentrations of C₂ through C₁₀ hydrocarbons in the water column beneath a slick only within the first 30 minutes after discharge. The highest observed concentration measured was 60 micrograms/liter 20 minutes after discharge. The maximum concentration corresponds with increased wind velocities and sea state when the spill occurred. A substantial portion of "dissolved" hydrocarbons in the water was likely separate-phase dispersed oil. The evidence shows that the concentration distribution of hydrocarbon species in the water was similar to that of the remaining slick.

The most volatile and toxic hydrocarbons, such as benzene and toluene, are the most soluble in the water column. Volatile compounds also evaporate rapidly, however. To test the relative importance of evaporation and dissolution in the removal of hydrocarbons from slicks, concentrations of benzene and cyclohexane were compared.³⁸ Benzene and cyclohexane have similar vapor pressures, 95.5 torrs for benzene and 97.8 torrs for cyclohexane. Therefore, benzene and cyclohexane should have similar evaporation rate constants.³⁸ The solubilities are quite different, 1,780 micrograms/liter for benzene and 55 micrograms/liter for cyclohexane. Concentrations of components remaining in the oil showed no preferential removal of either benzene or cyclohexane, suggesting that evaporation dominates dissolution in the removal of volatile components from the slick. Harrison et al.⁴⁴ found dissolution rates for aromatic hydrocarbons (cumene) about 1 percent and for alkanes about 0.01 percent of their evaporation rate.

Dissolution is a chemical degradative process of significant magnitude only within the first hour after a spill (fig. 3). Although continuing for several hours, the process becomes insignificant relative to

evaporation. The environmental threat from the dissolution of various toxic hydrocarbons is limited to a short timespan.

DISPERSION

Dispersion, or o/w emulsion, is the incorporation of small particles or globules of oil from 5 micrometers to several millimeters in size into the water column. According to figure 3, dispersion begins soon after the oil is discharged and is most significant at ~10 hours. Once formed, the particles continue to break down and disperse throughout the lifetime of the spill. By 10² hours dispersion has overtaken spreading as the primary mechanism for distributing the spilled oil about its center of mass.

The NSO components with hydrophilic groups such as -COO (acids), -OH (alcohols), -CHO (aldehydes), -OSO₃ (sulfates), and -SO₃H (sulfonates) act as natural surface active agents. These surfactants have hydrophilic and hydrophobic groups in the same molecule, causing them to orient across the oil-water phase boundary. The surfactant concentration in a crude oil to some extent determines the surface area of the slick. High surfactant concentrations encourage the slick to break up, increasing the oil-water interfacial area.

Under natural open-water conditions, however, turbulence plays a more significant role in controlling dispersion. Forrester⁴⁵ conducted a thorough study of the dispersed oil distribution after the tanker *Arrow* spill off Nova Scotia, Canada. He related the break-up of oil particles to the turbulent energy spectrum as:

$$L^2 \cdot \frac{P(L)}{E(L)} = \text{constant (independent of } L)$$

where L is particle length; P(L), probability per unit time that a particle of size L will bisect; and E(L), spectral density of turbulent energy of wavelength L required to break the particle. The L² indicates spherical particles. The equation suggests that smaller, possibly more abundant, dispersed oil particles are associated with lower turbulent energy areas. Distribution analysis of oil particles with depth indicates that total oil concentration decreases with depth while the relative abundance of small particles increases. The peak in the spectral density of particle sizes shifts to smaller values of L with greater depth and lower energy. The horizontal distribution of oil particles 5 or 10 meters below the surface located the highest concentrations away from the source. Dispersion progresses as oil drifts from the source and is greatest in areas of high wave energy, especially the surf zone.

The increased oil surface area (as a result of dispersion) increases rates of dissolution and biodegradation. Natural or chemically induced dispersion soon after the oil discharge may result in high dissolved hydrocarbon concentrations in the water column for a short time. Cormack and Nichols,⁴⁶ however, could not produce acutely toxic concentrations even under controlled conditions immediately after discharge. Dispersed oil residues continue to disperse and degrade up to 10⁴ hours, subject to other long-term processes such as biodegradation and sedimentation.

EMULSIFICATION

Water-in oil (w/o) emulsions form a viscous cream, or floating, coherent semisolid lumps, often called

chocolate mousse. Oil is the continuous phase into which tiny water droplets about 15 micrometers in

diameter are incorporated. Like dispersion, w/o emulsification depends on oil composition and sea state.

The evaporation of volatile hydrocarbons within the first 10 hours after the oil discharge and subsequent increases in density and viscosity initiate the formation of w/o emulsions. The formation reaches a maximum between 10 and 10² hours (fig. 3). The asphaltene fraction of a crude (non-n-heptane extractable portion of the > 593°C fraction) contains emulsifying agents studied by Mackay et al.⁴⁷ These emulsifying agents are essential for the formation and stability of w/o emulsions. The abundance of the agents largely determines the type of emulsification, w/o or o/w (oil-in-water = dispersion). Although the exact chemical nature of the emulsifying agents is not understood, percentages of hydrogen, carbon, nitrogen, sulfur, and oxygen are close to that of the asphaltene from which they are extracted (table 5).

	Venezuelan asphaltenes, %	Extracted emulsifiers, %
Nitrogen	1.4	1.3
Carbon	86.2	86.1
Hydrogen	7.8	7.8
Oxygen and sulfur	4.6	4.8

Table 5. The elemental analysis of stabilization agents in the Venezuelan asphaltene fraction and extracted emulsifiers (from Mackay et al.⁴⁷).

Sea state influences the formation rate of o/w emulsions but apparently does not affect the ultimate extent of emulsification. The turbulent energy of a gently rolling sea is enough. Cresting and sea spray involve turbulence many times greater than that required for emulsification. Studies show the ubiquity of w/o emulsions with oil and water phases.

The water content of a w/o emulsion is commonly 80 to 90 percent. The ultimate water content (extent) of emulsion is independent of turbulence. However, the water and asphaltene content of the oil affect the physical character of the emulsion. Higher water and/or asphaltene content result in greater density and viscosity.

Emulsification is virtually an irreversible process impeding cleanup tactics such as dispersion, ignition, and skimming. Emulsification inhibits the degradation and weathering of petroleum by limiting the amount of exposed surface area free to exchange with the open water and atmosphere. Water trapped inside of a w/o emulsion is not voluminous enough to provide sufficient oxygen and nutrients for extensive degradation.⁴⁸ Microbial degradation, autooxidation, photo-oxidation, and dissolution processes (in order of decreasing magnitude) continue to alter and destroy the residues. Emulsions persist for more than 10⁴ hours as pelagic tar noted for washing ashore or accumulating in current gyres and convergence zones. The degradation, weathering, and incorporation of detrital or biogenic skeletal material into emulsions increase the specific gravity enough to cause the emulsions to sink or disperse throughout the water column.

SEDIMENTATION

Increasing the specific gravity of petroleum or petroleum residues over that of seawater (1.025) results in sedimentation of the petroleum substance. Three dominant types of processes act on floating and dispersed oil to increase its specific gravity: adhesion onto suspended detrital materials, sorption of

dissolved species onto suspended particulate matter, and increased specific gravity (because of evaporation and dissolution).

Perhaps the dominant sedimentation cause is adhesion of the petroleum to detrital mineral particles

(suspended silts and clays) or to the exoskeletons of planktonic protozoans and algae. Common detrital minerals have specific gravities of 2.5 to 3.0 and can effectively sediment several times their volume in petroleum. The specific gravity of crudes ranges from about 0.82 to 0.92. Adhesion is the principle behind using sinking agents for the removal of floating oil from the water surface.

Several studies have shown that suspended material can absorb or adsorb large quantities of dissolved hydrocarbon species from the water column.^{49,50} Because of their large surface area/volume ratios and electrochemical properties, fine-grained clay minerals (< 44 micrometers) have the greatest sorption capabilities of any material in the sedimentary spectrum. Bentonite and kaolinite are the most absorptive common marine minerals, followed by illite, montmorillonite, and calcite. Hydrocarbon sorption by mineral particles is inhibited in the presence of indigenous organic materials and is positively correlated with salinity.⁵¹

These two sedimentation types, adhesion and sorption, vary considerably from place to place. Both depend on the amount and type of particulate matter in the water column. Sedimentation increases in shallow, nearshore areas where runoff-borne or storm-resuspended sediments result in particulate loading in the water column and high turbidity. The varying geochemical nature of suspended sediments, largely due to provenance, affects sedimentation.

Other sedimentation processes deplete the petroleum in lighter weight fractions by evaporation, oxidation, and dissolution. Autooxidation, photooxidation, and biological oxidation yield acids, alcohols, hydroperoxides, and phenols considerably more soluble than the hydrocarbons from which they were derived.⁵² These are all degradative processes within themselves, but physical and chemical

alterations are interdependent. Oils with higher specific gravities initially tend towards simple sedimentation of their weathered residues.

The fate of petroleum or petroleum hydrocarbons once sedimented varies according to local conditions. Important factors influencing petroleum dispersal in sediments are the energy regime, sedimentation rates, quantities of hydrocarbons sedimented, bioturbation, and sediment or substrate properties. Thorough documentation of sediment-petroleum interactions in various depositional environments is not available. Petroleum residues and sorbed hydrocarbons persist for years in the sediments in a dynamic, slow degradation state. Oils stranded along shorelines are subject to the most severe weathering conditions under intermittent subareal exposure and high wave energy conditions. Vandermeulen and Gordon⁵³ postulate that on a low-energy sandy beach dissolution of hydrocarbons after autooxidation or biological oxidation occurs through interstitial water and these dissolved species are not introduced into the littoral waters. Oil stranded on low-energy beaches is more likely buried with little chance of reexposure. A high-energy beach profile undergoes drastic changes with seasons or a major storm. Petroleum is frequently buried, reexposed, and reintroduced into the littoral environment.

In nearshore areas below the storm wave base and in offshore continental shelf areas, physical conditions are less extreme. Sedimented petroleum is dispersed laterally by seasonal or permanent currents. Bioturbation results in the vertical dispersion of hydrocarbons throughout the upper centimeters of the sediment column. Otherwise, residues and hydrocarbons persist, undergoing biodegradation while normal sedimentation processes bury the oil. Meyers⁵⁴ concluded that sediments act as a sink for petroleum hydrocarbons, effectively isolating them from further environmental interaction.

BIODEGRADATION

The first processes acting on a spill are all physical, involving distribution of the oil and partitioning of its

components among the sea surface, air, water column, and sediments. Physical weathering greatly alters the

destructive potential of an oilspill by changing its physical properties, redistributing toxic components, and determining its location. After extensive alterations, however, many petroleum hydrocarbons persist unchanged. Their toxic nature is diluted but not diminished. Petroleum residues, asphaltenes, and nonvolatile hydrocarbons persist indefinitely. At a critical time about 10^2 hours after a spill, the biological and chemical degradative processes become increasingly significant (fig. 3). Because marine microorganisms and macroorganisms ingest, metabolize, and utilize the petroleum as a carbon source, petroleum hydrocarbons and residues in the environment do not exist in greater abundance. Without the organisms the abundance would increase at possibly undesirable rates.

The rate and extent of biodegradation depend on the nature and abundance of the indigenous microbial assemblage, predators, available inorganic nutrients and oxygen, ambient temperature, and oil distribution and composition. The water depth and the presence or absence of oil in the sediment or water column may also be significant factors.

Several studies have demonstrated the ubiquity of hydrocarbon-utilizing microbes in the waters and sediments of the world ocean and in freshwater.⁵⁵⁻⁵⁹ Petroleumlytic microbes are commonly more abundant in chronically polluted waters than in more pristine waters.^{56,60} In the North Sea, Oppenheimer et al.⁵⁸ noted a distinct dominance of oil-degrading bacteria in the water column and sediments near the most active Ekofisk production field and Elbe River mouth in West Germany, presumably contaminated by the industrial and municipal discharge of petroliferous waste. Another recent study noted marked differences in microbial diversity and abundance between a chronic natural seep area and adjacent uncontaminated water.⁶¹

Organisms able to use and degrade hydrocarbons include 28 known genera of bacteria, 12 of yeast, 30 of filamentous fungi,⁶² and at least one alga.⁶³ All types are not omnipresent in the oceans, nor do they all attack the same oil components. Therefore, the

biodegradative effects depend on the specific assemblage available. Conversely, in spite of the indigenous assemblage available, crude oil composition influences specifically which petroleumlytic microbes are most active.⁶⁴ In comparing two crudes and two fuel oils, Walker, Petrakis, and Colwell⁶⁵ found that low-sulfur and high-saturate content were conducive to biodegradation. Aromatics and n-paraffins seem to be the most readily utilized hydrocarbons, although other components can support microbial activity. Jobson et al.⁶⁶ suggest that cooxidation with n-paraffins occurs in the metabolism of aromatics because they are not readily metabolized as the sole carbon source.

Recent studies have shown the occurrence of sequential bacterial growth on crude oil. The dominant microbial assemblage acting on the petroleum and metabolite types produced vary with time according to the oil composition.⁶⁷ Pure cultures possibly can metabolize petroleum faster for portions of a complete degradative sequence, but the biodegradative extent is limited when the entire microbial sequence does not develop. Initial biodegradative activity on a whole crude oil selectively degrades n-paraffins and, to a lesser extent, aromatics.⁶⁶ The metabolic products of this early stage are probably NSO compounds which increase the specific gravity of the crude and enhance the formation of o/w emulsions.⁶⁸ This activity increases the surface area of the oil, increasing the available hydrocarbons, and permits continuing exponential bacterial growth.

Degradation of weathered crudes and fuel oils 2 and 6 may be dominated by a different microbial assemblage. Independent studies noted the metabolic production of new, higher molecular weight (C^{20} to C^{23}) n-alkanes during this phase.^{67,69} These unnatural n-alkanes are similar to some pelagic tar components, indicative of the ultimate fate of petroleum residues. Biodegradation of crude oils with microbial populations enriched on more weathered oils, in sequence or in a mixed culture with an early phase assemblage, yielded over 75 percent conversion of the petroleum to nonextractable (benzene-pentane-diethyl

ether) form under laboratory conditions.⁶⁷ Similar studies did not find the biodegradation so extensive but greater than 50 percent for initially unweathered crudes.⁶² Microbial populations influence biodegradation rates with other critical parameters, such as temperature and oil composition. But the populations probably do not limit the biodegradative extent.

Concentrations of inorganic nutrients (PO_4 , NO_3 , NO_2 , and NH_4) and dissolved oxygen (DO) in seawater can limit biodegradation. Conflict exists in the literature on the relative significance of nitrogen and phosphorus as limiting factors. Gibbs⁴⁸ and Gibbs et al.⁷⁰ determined that nitrogen supply controlled oxidation rates. A Q_{10} value (the ratio of oxidation rates at 14 and 4 °C per unit nitrogen uptake) of 2.7 was obtained under experimental conditions. This difference in oxygen/nitrogen demand ratios may reflect a change in the balance between microbial respiration (CO_2 production) and protein synthesis for the biomass production. Mulkins-Phillips and Stewart⁵⁵ determined that nitrogen replenishment in marine waters prevents nitrogen from limiting the rate or population at normal biodegradation rates. In their study, however, phosphorus limited the growth rate and population size of a pure *Nocardia* sp. culture. Limitation by either essential nutrient is more likely in open oceans than in inshore areas of high terrestrial runoff.

Under normal marine conditions, DO levels are unlikely to drop low enough to be a limiting factor. Near the surface, turbulent exchange with the atmosphere maintains DO at near saturation levels. Severely depleted oxygen levels probably occur only in bottom sediments or in small restricted basins, such as lakes or estuaries, extensively covered by oil.

Studies of oil biodegradation in arctic environments or comparative studies of moderate and cold (< 10 °C) conditions in laboratory studies confirm^{57,71-73} that biodegradation rates are consistently slower in cold waters. Ward and Brock⁵⁷ cited temperature, rather than nutrients, as the rate-limiting factor during fall, winter, and spring in a temperate

lake. Several studies also noted a substantially longer lag phase before the exponential growth rates begin. Contrarily, Atlas⁷⁴ observed no significant lag phase during microbial degradation of Prudhoe Bay crude oil under moderate (25 °C) and/or cold (5 °C) laboratory conditions. Such a phenomenon is characteristic of the biodegradation of weathered crudes, heavy crudes, and refined products such as fuel oils. Apparently, the low-boiling fraction of most oils contains bactericidal or bacteriostatic hydrocarbon components. At moderate temperatures, evaporation and solution remove these toxic components before biological activity begins. Lower solubility and evaporation rates at lower temperatures allow these components to persist, resulting in a growth lag.

Oil trapped in ice is isolated and preserved indefinitely. Gibbs⁴⁸ calculated that, based on its nitrogen content, 1 liter of seawater is required to oxidize 2.5 milligrams of Kuwait crude (about 3 microliters). In frozen seawater, insufficient circulation or diffusion exists to biodegrade any oil.

The microbial degradation of oilspills can be enhanced by: 1) dispersion with nonbactericidal dispersants, 2) seeding with freeze-dried or slurried assemblages of petroleumlytic microbes to supplement the indigenous population and hurry the onset of exponential growth, and 3) fertilization with oliophilic mixtures of nitrogen, phosphorus, and possibly iron.^{75,76} Current research on the specific biodegradative capabilities of specific microbes, development of more effective strains, and other research may lead to the development of optimum seed populations for highly specific conditions of temperature and oil composition.^{63,64,75}

The development of nutrient fertilizers is a recent, well-developed field. Various nitrogen- and phosphorus-containing salts, either naturally oliophilic or rendered oliophilic by solution in a paraffin base, enrich the available nutrient supply in an oil slick. Olivieri et al.⁷⁶ prefer their paraffin-supported fertilizer in which the bioactive salt is $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$. The advantages of this single salt solution are: its low solubility, resulting in a slow

release effect; assured balanced release of the two nutrients; and nontoxicity. Dibble and Bartha⁷⁵ found that the addition of chelated ferric iron in iron-depleted waters could be responsible for substantial increases in biodegradation rates.

Seeding and fertilization are useful secondary cleanup techniques to speed removal of material missed or unrecoverable by skimmers. Biodegradation rates of 71 percent removal within three days were reported after fertilization. Rates vary considerably, depending on many other parameters.

Seeding and fertilization of an oil slick may result in blooms. Besides altering the ecosystem balance, such prodigious microbial activity produces corresponding quantities of metabolites with undetermined potentially toxic effects. Significant accumulation of such metabolic products, primarily fatty acids and alcohols, is unlikely in the open sea but possibly significant in a restricted area.

The sorption, weathering, and degradation of petroleum increase its specific gravity and result in sedimentation. Oil residues and petroleum

hydrocarbons in sediments continue to be degraded by aerobic microbes, although less rapidly than in the water column.⁶³ Walker and Colwell⁵⁹ found petroleum contamination of sediments reduced by 75 percent one month after a spill. Some contamination is probably lost to the water column without microbial interaction.⁷⁷ Recent studies^{65,78,79} demonstrated that barophilic deep-sea sediment bacteria can degrade organic materials and hydrocarbons more rapidly than shallow-water sediment bacteria at surficial pressure.

Anoxic conditions commonly exist in subsurface sediments and even at the sediment/water interface in basins with restricted circulation. These conditions inhibit the biodegradation of petroleum residues and hydrocarbons. Research attributed the catalysis of anaerobic oxidation of various hydrocarbons by sulfate reduction to *Desulfovibrio* species.⁸⁰ Laboratory studies showed that under anaerobic conditions in the presence of sulfates, petroleum products are lost more rapidly than aromatic and aliphatic hydrocarbons. The rate and extent of anaerobic biodegradation in subsurface sediments usually depends on the diffusion rate of toxic compounds which are the oxidation byproducts.

AUTOOXIDATION

Autooxidation is the degradative process of hydrocarbons in floating and dispersed oils reacting with oxygen molecules in the water column. The extent and products of oxidation reactions vary depending on petroleum properties and composition, water temperature, solar radiation intensity, abundance of various inorganic components in the water or oil, and extent of diffusion and spreading of the oil. Weathering processes, such as evaporation and dissolution, act more rapidly than oxidative reactions to remove essentially all the hydrocarbons more volatile than n-C₁₅ and a smaller percentage of the less volatile components (fig. 3).

Oxidative reactions follow one of two principal pathways. The most commonly studied is the oxygenation or dehydrogenation of paraffins or alkyl groups on cycloalkanes and aromatics, resulting in the

successive formation of alcohols, aldehydes, or ketones, and finally carboxylic acid. Hansen⁸¹ determined that alcohols, aldehydes, and ketones are short-lived, intermediate compounds rapidly oxidized to yield acids. These acids are rapidly dissolved into the water. Free radicals produced in the decomposition of impurities or by photolysis begin the oxidation which proceeds as a free radical chain reaction. Dissolved metal ions of variable valence, such as vanadium, a trace metal common to petroleum, act as catalysts, influencing the initial reaction rate. Sulfur compounds, however, inhibit complete autooxidation to carboxylic acid by causing chain-terminating reactions. Acid formation by oxidative degradation increases the solubility of hydrocarbon components and effectively degrades petroleum.

The other oxidative pathway is the formation of higher molecular weight compounds either by polymerization of radicals and condensation of aldehydes and ketones by phenols or by esterification between alcohols and carboxylic acids.⁸² The predominance of these reactions over oxidation and solution of the carboxylic acid results from the inhibited diffusion of oxidation products to the oil-water interface. High viscosity and/or low surface-area-to-volume ratios encourage the formation of persistent tarry residues rather than degradation.

The opaque nature of the tar inhibits the photo-oxidation of tarry residues or petroleum globules with a tarry crust.

The types of hydrocarbon groups in an oil influence the extent and rate of autooxidation. Hansen⁸¹ concluded that a fourfold increase in the relative percentage of aromatics from crude to oxidation products showed preferential degradation of the aromatic compounds. Alkylated hydrocarbons oxidize more easily because the tertiary C-H bonds are weaker than primary or secondary C-H bonds. Consequently, normal alkanes are the least susceptible to autooxidation.

Besides influencing the solubility of components from an oilspill, oxidation enhances dispersion and emulsification. The chain-breaking reactions of sulfoxide formation generate surfactants, enhancing the formation of o/w emulsions (dispersions). This process contributes more toward slick degradation than the simple formation of water-soluble oxidation products.

Photosensitizing compounds, for example, 1-naphthol, increase hydrocarbon oxidation rates.⁷⁸ Such treatment of oil slicks must be used with discretion because of the widely differing possible results. Photosensitive additives applied to low-viscosity slicks can significantly assist petroleum degradation. However, their addition to high-viscosity or weathered slicks may cause the slick to contract and congeal into a floating tar mass slow to degrade.

Autooxidation rates are prohibitively complex to calculate because of the various controlling conditions and multiple pathways for degradation reactions. Although perhaps worthy of future research, oxidation processes are not particularly critical in dealing with oilspill cleanup. More rapidly acting physical processes require immediate attention.

CONCLUSION

Effective cleanup efforts are contingent on a good estimate of the dominant physical, chemical, and biological processes acting on the spill at any given time. The physical processes dominate earliest with spreading as the most critical. Intermediate-time processes, such as evaporation, emulsification, and dispersion, alter the composition and physical state of the oil. Sedimentation and biodegradation largely determine the ultimate fate of the oil and may be active for years after the spill. Some processes such as drift may be equally important immediately after or several months after the spill.

Predictive modeling studies are now an important research area on the fate of oilspills. Some modeling attempts are more successful than others, but the

complexities of weathering and degradation processes limit their accuracies to good first approximations. Parameters controlling processes are interrelated and critically dependent upon environmental factors and initial oil composition. Needed research includes:

1. The formulation of a unifying theory for slick drift specific for viscous surface film movement. An accurate definition of each physical parameter, such as wind drift, wave transport, and current drift, is one of the most demanding research areas.
2. A model of evaporation from slicks of specific composition under various environmental conditions. Many factors depend on slick composition and physical properties.

3. New methods for retarding emulsification or new technology for removing emulsions and pelagic tar from the water. These developments would reduce the risk of nearshoreline damage. The formation of w/o emulsions inhibits cleanup.

4. The fate of oil and petroleum residues reaching the bottom sediments. Are the residues isolated, redistributed, or degraded?

5. The alteration of petroleum components by photo-oxidation, autooxidation, and biooxidation. Some suggest that this alteration may yield potentially toxic or carcinogenic intermediate or final products. If so, the accumulation of such products could be significant in chronically polluted water bodies. This is a currently active research area.

6. The development of microbial inocula for the treatment of spills under specific conditions to optimize biodegradative processes. The factors for consideration include slick composition and environmental conditions.

7. The synthesis of knowledge on the fate of oilspills into risk analyses (appendix). Models for the movement and deterioration of oil slicks with data on the spill probability and severity of economic and ecological impact should be used to derive risk maps of shorelines. Similar studies have already been conducted by the U. S. Geological Survey (U.S.G.S.)¹⁹⁻²² for U. S. shorelines adjacent to proposed OCS lease areas. The scope of these studies, however, was limited to prospective offshore production and did not include risk factors of tanker traffic.

Natural weathering and degradative processes effectively and rapidly reduce the destructive potential of oilspills. In addition to physical methods of containment and cleanup of spills, which remain the primary defense, some success in controlling spills has been achieved by enhancing and accelerating natural processes by chemical dispersion, burning, and biodegradation.

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APPENDIX

A COMPREHENSIVE OILSPILL RISK ANALYSIS FOR
U. S. COASTAL WATERS

Oilspill risk analysis has become critical in the environmental impact assessment for the exploitation of OCS petroleum. The U.S.G.S.¹⁹⁻²² has completed thorough risk analyses for several OCS lease areas. Other groups have compiled thorough risk estimates for the offshore storage and transportation of OCS oil.⁸³

Vast national coastlines have not been modeled yet. Areas modeled have been limited to particular aspects of oilspill risk. The synthesis of available analyses with further studies to cover the Atlantic, Pacific, Gulf of Alaska, and Gulf of Mexico coasts could yield valuable information for oilspill contingency planning. Performing such an analysis for the continental U. S. coastline requires the compilation and reduction of much data.

The first area of risk analysis is the determination of spill probability. Five categories comprise the probability: tanker spills, transmission pipelines, offshore storage, offshore exploration, and offshore production. Large-volume oilspills include greater than 160 meters³ and small-volume spills include less than 16 meters.³ The small-volume spills usually result from loading and unloading operations.

From OCS production areas petroleum is transported in three ways.⁸⁴

1. **Tanker transshipment** — Temporary oil storage at the production site, transport to shore storage by small shuttle tankers ($\sim 2.6 \times 10^7$ deadweight kilograms), and transfer to 9.2×10^7 -deadweight-kilogram tankers for long-distance transport.
2. **Pipeline transshipment** — The pumping of oil by pipeline directly from the production site to shore storage, where it is transferred to 9.2×10^7 -deadweight-kilogram tankers for long-distance shipment.

3. **Direct shipment** — Oil storage temporarily offshore and transfer directly to 9.2×10^7 -deadweight-kilogram tankers for long-distance shipment.

Three types of risk elements, tanker transport, pipeline transport, and storage, collectively determine the risk in each transportation system. Even without OCS production and exploration, the transportation of petroleum and petroleum products by tankers in coastal waters may be an important factor.

Donovan and Owen⁸⁴ outlined three categories of potential oilspills from tanker traffic:

1. Large spills by ramming or collision. Ramming and collision frequency data are available for most major U. S. ports.^{85,86} Reasonable estimates may be made for new locations based on existing data.⁶ About 10 percent of the rammings and collisions result in major oilspills.⁸⁷ Of these, about 10 percent result in the total loss of the vessel and entire contents. For 90 percent of the major spills, 60 percent of the vessel capacity is lost. Donovan and Owen⁸⁴ calculated a weighted average of 65 percent of tanker capacity for major spills.
2. Large spills from groundings, fires, explosions, mechanical breakdowns, structural failures and tsunamis (in the Gulf of Alaska). Worldwide spill frequency, magnitude, and total spill volume may be calculated.⁸⁸ The U. S. Coast Guard (U.S.C.G.) data for spills in U. S. waters probably better represents the actual frequency than worldwide data because of reluctance of tanker operators to report spills. From this comprehensive data, ramming and collision spills must be deducted. Card et al.⁸⁷ estimate that rammings and collisions cause about 21 percent of the total spill volume.

3. Small spills from operations at offshore single-point moorings and onshore terminals. Baseline spill frequencies are available for these operations¹¹ and may be modified to accommodate local operations.

The trans-Alaska pipeline project has fostered technological improvements in pipeline transportation. Modern pipeline leak-detection systems (pressure deviation, flow deviation, and line volume balance) have significantly limited the maximum possible outflow for an accident. Devanney and Stewart⁸⁸ gave data for spills greater than 160 meters. Owen et al.⁸³ concluded that pipeline, instead of tanker transmission, cannot be used universally because of the variations among sites.

The oilspill risk must be determined for three tank storage types: onshore, floating, and ocean floor. Onshore oil storage presents little threat to the water with standard construction precautions and avoidance of natural hazards. Owen et al.⁸³ determined that the risk of ocean floor storage is 60 times greater than of floating storage tanks. Each site must be evaluated independently.

Offshore exploration primarily includes blowout risks during drilling. Bercha⁸⁹ determined the probabilities of oil blowouts in the Beaufort Sea. The risk factors include human error, design, equipment performance, geology, environment, and anomalies. The most controllable factor is human error.

Oilspill probabilities for offshore production are based on historical data on spill frequencies. Researchers assume that the frequency does not vary with geographic location and that the oilspill probability is proportional to the oil volume produced and handled. The U.S.G.S. studies^{19,21,22,29} used Devanney and Stewart's⁸⁸ model for statistical frequency distributions. According to Slack and Smith²⁰, the U.S.C.G. data on spillage rates from production platforms and pipelines showed no significant improvement from 1971 to 1975.

After the spill probability has been calculated with all pertinent factors for an area, spill trajectories must be modeled. For risk analysis, the best approach is a Monte Carlo simulation of many hypothetical spills under varying conditions, such as seasons.⁹⁰ The result is summarized statistically as a probability distribution of the possible locations of an hypothetical spill at any time.

The modeling of hypothetical trajectories can identify high-risk shorelines. High-risk areas should be evaluated for the environmental impact of an impinging oilspill on coastal biological, commercial, and recreational resources. Typical resources include sandy beaches, recreational areas, wildlife refuges, historical sites, nesting sites, rookeries, commercial fishing grounds, and breeding grounds. Cleanup operations should be outlined for areas where spills could severely damage coastal resources. The vulnerability of some resources varies monthly or seasonally depending on spawning or other cycles.