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Impact of Petroleum Spills
on the Chemical and Physical Properties
of the Air/Sea Interface

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CONTENTS

Abstract	ii
Problem Status	ii
Authorization	ii
PROLOGUE	1
SPREADING AND DISTRIBUTION OF SPILLED OIL	1
INFLUENCE OF NATURAL FORCES ON OIL AT SEA	3
INFLUENCE OF OIL FILMS ON PROPERTIES OF THE AIR/SEA INTERFACE	5
Wave Damping	5
Gas Transport	7
Exchange of Solids and Liquids	8
EXTENT OF OIL IN THE OCEANS AND ON ITS SURFACE	11
SUMMARY AND CONCLUSIONS	13
REFERENCES	13

ABSTRACT

Oil on the sea spreads rapidly under the influence of wind, surface currents, and hydrostatic forces and attains a crude equilibrium with thin films containing large quantities of surface-active constituents. The time required to reach this condition depends on the spill volume, the meteorological conditions, and the character of the oil. Several natural forces operate on the oil slick to disperse its constituents into the marine environment. Weathering, dispersion, and air/sea dynamics ultimately degrade the spill to tarlike lumps and/or stable water-in-oil emulsions, both which have long lifetimes in the sea.

Layers of petroleum oils and their attendant monomolecular films influence various properties of the air/sea interface and modify exchange processes between the atmosphere and the ocean. Capillary waves are resisted and attenuated, and the interaction between wind and waves is uncoupled through the elimination of form drag. Gas exchange may be inhibited by oil films, but this effect does not occur to a serious extent in the open ocean. Liquid and solid exchange is altered, organic fallout is concentrated at the surface by the oil, and oil is transported into the marine atmosphere. Contaminant oils replace a high-surface-tension, active water surface with a more phlegmatic, less mobile organic/air interface. Although an oil slick can damp its environment by slowing processes at the air/sea interface and resisting interactions between the ocean and atmosphere, a worldwide ocean surface film, capable of global environmental impacts, is unlikely.

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IMPACT OF PETROLEUM SPILLS ON THE CHEMICAL AND PHYSICAL PROPERTIES OF THE AIR/SEA INTERFACE

PROLOGUE

The influence of an oil spill on the sea surface and the adjacent atmosphere can be assessed through an integration of the many boundary processes that are altered by this complex mixture of chemicals. The problem is multidisciplinary and involves an evaluation of the effects of a mixed organic layer on a dynamic undulating water surface whose chemical composition is constantly being modified by physical, chemical, and biological processes. To address systematically the net effect of an oil spill, it is necessary to consider its chemical and physical character, magnitude, mode of spreading, distribution on a wave-covered surface, and the dispersive forces of the marine environment which selectively remove portions of the spill from the sea surface. The influence of an oil layer and its attendant monomolecular film on the microscale properties and exchange processes at the air/sea interface will be extrapolated to larger-scale effects on the marine environment.

SPREADING AND DISTRIBUTION OF SPILLED OIL

To properly assess the influence of oil at the air/sea interface, its area of coverage, thickness, and physical condition must be determined as a function of time. Fay (1) considered the spread of oil onto a calm sea and concluded that gravitational effects controlled spreading in the initial stages of a spill. Other factors dictate spreading characteristics as the oil layer thins; for example, consider a typical crude oil where the water surface tension is 30 dynes/cm and the oil-water density difference is 0.05 gm/cm^3 . In this situation surface forces take control of the spreading process once the oil has thinned to 0.8 cm thickness. It was concluded that for most spills, after the first hour or two, slick size was controlled by a surface tension-viscosity relationship which was independent of spill volume. In actual field experiments involving spilled oil, the area occupied by the slick increases rapidly under the influence of both hydrostatic and surface forces. This area eventually becomes constant as further enlargement is limited and offset by natural dispersive forces, an aspect to be considered subsequently in this report.

As more data on accidental spills become available, it is apparent that even the viscous crudes spread rapidly into thin layers which come under the influence of surface effects. For example, Berridge (2) et al., using an equation derived by Blokker (3), calculate that 100 m^3 of various crudes will thin to an average value of 0.055 cm after only 17 min, 0.012 cm after 3 hr, and 0.003 cm (30μ) after 28 hr. Even the great spills of the last few years eventually decreased in thickness to a point where surface forces would determine their characteristics. Allen (4) estimates a minimum average thickness of 0.0025 cm for the Santa Barbara incident, assuming that spreading had occurred for 24 hr. Similarly, Smith (5) estimated that the oil slick measuring 10 by 40 miles which was observed 6 days after the Torrey Canyon stranding would have had an average thickness of 0.003 cm, a value strikingly similar to many of the estimates reported thus far in this report.

Thus, even the massive spills eventually spread into thin layers, not only by the spreading mechanisms but also through the action of the manifold natural dispersive forces which act to remove oil from the water surface. It should also be noted that these thickness estimates are averages. Once a spill has thinned and surface forces begin to play an important role, the oil film is no longer continuous and uniform but becomes fragmented by wind and waves into islands and windrows.

The influence of surface forces on the spreading of thin oil films becomes increasingly important as a spill spreads. Most pure hydrocarbons, the major component of petroleum products, do not spread spontaneously onto a water surface. According to Langmuir (6), the thickness of a large lens of nonspreading oil on water can be calculated from

$$t^2 = \frac{-2F\rho_w}{g\rho_o(\rho_w - \rho_o)}, \quad (1)$$

where

t = oil lens thickness

ρ_o = oil density

ρ_w = water density

F = spreading pressure (dynes/cm).

Hydrocarbons with low molecular weights do not remain as a liquid lens but spread readily and exert a positive spreading pressure (7). The spreading pressure of the oil F_o is defined as

$$F_o = \gamma_w - (\gamma_o + \gamma_{ow}), \quad (2)$$

where

γ_w = surface tension of water

γ_o = surface tension of oil

γ_{ow} = interfacial tension between the oil and water.

Most aromatic and aliphatic hydrocarbons more volatile than n-nonane have small positive F_o values (spread), while none of the cyclic hydrocarbons spread spontaneously; i.e., their spreading pressures are negative. When petroleum spills occur, the volatile, rapidly spreading components evaporate, leaving behind a complex mixture of the higher-molecular-weight hydrocarbons and compounds containing oxygen and sulfur. The principal hydrocarbon families in crude oils are the alkanes, cycloparaffins, alkenes, and aromatics. The sulfur- and oxygen-containing compounds are surface active; the hydrophilic polar portion of the molecule is associated with the water surface and the nonpolar or hydrocarbon portion is oriented toward the petroleum oil. These surface-active constituents cause the otherwise nonspreading hydrocarbon oils to thin out into expanded slicks surrounded by thin films which approach monomolecular dimensions. The extent of spreading is a function of the quantity and nature of the surface-active components of the oil.

If the water surface is already occupied by a surface film (natural sea slick or man-made pollutant film), spreading of the oil may be retarded. Further, surface currents driven by wind, waves, and convectional cells determine the shape and direction of movement of the oil spill, wind being the most influential external factor (3). The spreading tendency (spreading pressure) of the oil against external forces depends on the quantity

of surface-active material in the oil. For example, mixtures containing 0.2, 0.5, and 1.0% of 1-dodecanol dissolved in nonspreading paraffin oil ($F_o < 0$) gave positive spreading pressure values of 3.0, 11.0, and 17.5 dynes/cm respectively. (8).

For small spills and larger ones which have aged, most of the oil will be found in the thicker layers which are in equilibrium with thinner peripheral films. In studying the chemical and physical effects of oil on the air/sea interface, we must consider the monolayers formed from the rapid spreading of its surface-active constituents as well as the thicker layers formed by patches of oil that have not spread extensively. In small spills the area occupied by a thin surface film can be quite large when compared to that covered by the bulk of the oil, and estimates of spill volume may be greatly in error unless the thick films can be differentiated from the monomolecular layers and their thicknesses determined. For example, if ideally distributed, only 1.5 gallons of a pure surface-active material, such as oleic acid, is required to cover a square mile of water surface with a monomolecular film and produce an obvious slick (9). This one-molecule-thick film is visible on a body of water as a light reflectance anomaly due to the absence of capillary waves. For this reason a visible slick on a body of water does not necessarily represent a large quantity of pollutant, but may be a well-spread film of highly surface-active oil. Consequently, remote sensing systems for oil spills and other water-surface pollution must be calibrated in the field in concert with appropriate ground truth.

INFLUENCE OF NATURAL FORCES ON OIL AT SEA

Nature's compound attack on oil at the sea surface has thus far prevented the ocean from becoming wholly covered with pollutant slicks and films. There are a number of dispersive processes which act on this floating organic contamination (Fig. 1) to partially destroy and disperse it into the subsurface marine environment and, to a lesser extent, into the marine atmosphere. Volatile, low-molecular-weight constituents of an oil slick evaporate quickly leaving behind a more viscous, denser residue. For example, Kinney et al. (10) found that evaporation from a crude oil in Cook Inlet, Alaska, effectively removed hydrocarbon components as volatile as n-decane within 8 hr. The evaporative process is enhanced by both winds and thinning of the film through spreading. Distillate petroleum products such as fuel and lubricating oils have few volatile constituents and are less altered by loss of their light ends. In addition to evaporation, liquid oil may be transported into the marine atmosphere by wind-generated sea spray or by fragments from bursting bubbles (11,12).

Pathways for oil-slick components into the sea include dissolution of water-soluble substances, adsorption onto nonbuoyant particulate matter, and emulsification caused by the physical action of waves and breaking water. Heavy crude oil may sink after the loss of volatile constituents which causes the density of the remaining oil to exceed that of the surface water. In addition, constituents of the sea surface are forced into the sea by sinking water motions beneath wind-driven film streaks or windrows (13). Emulsification is enhanced by the presence of emulsion-stabilizing, surface-active compounds in the oil. This process may take two forms: oil-in-water emulsion, where the sea is the continuous phase, or water-in-oil, where the stable floating emulsion contains 30 to 80% water. According to Berridge et al. (2) the latter form does not require the addition of external dispersing agents but forms naturally on a dynamic sea surface. It is likely that the generation of this type of emulsion requires violent agitation at the air/sea interface and relatively thick oil films. Unstable oil-in-water emulsions occur with lighter petroleum distillate products when stresses at the sea surface force oil into water as small drops. Emulsification of crude oil into seawater

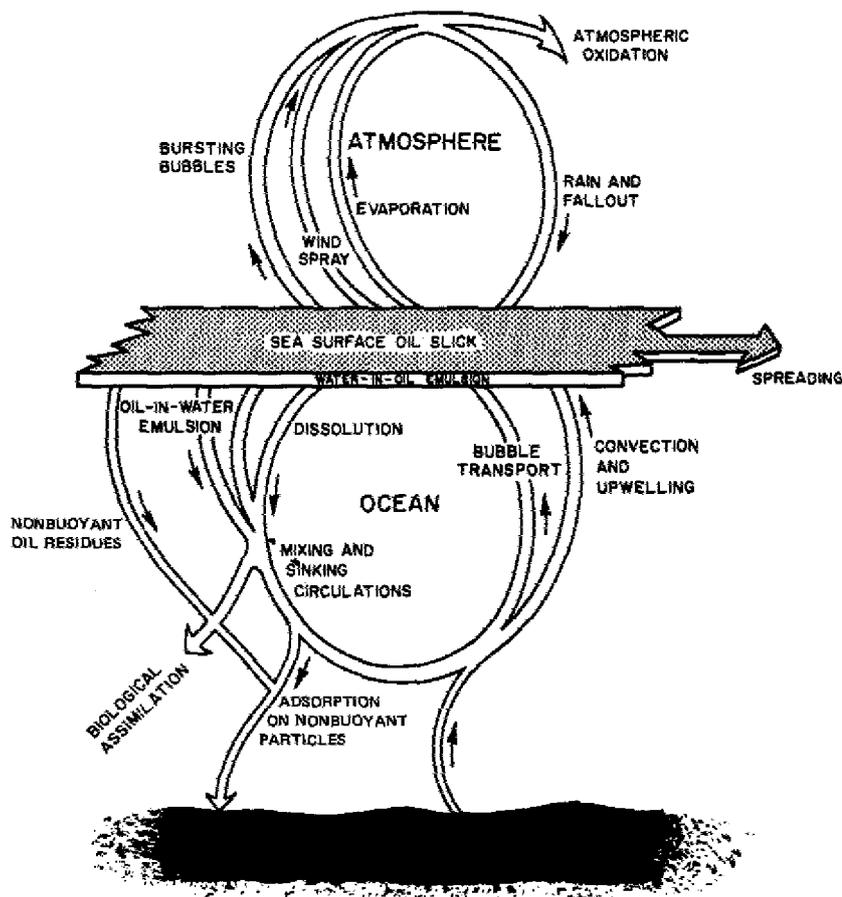


Fig. 1 — Natural forces which disperse and modify oil slicks on water

may also be promoted by surface-active materials produced during degradation of the oil by certain microorganisms (14).

Decomposition and chemical alteration of portions of a sea-surface oil slick can result from atmospheric oxidation and ultraviolet attack. Paraffins and aromatic hydrocarbons with tertiary C-H bonds are most readily attacked by oxygen through an autooxidative process (2). In thin films and monolayers chemically unsaturated species are prime subjects for actinic attack. This photochemical oxidation ultimately breaks the unsaturated molecules into smaller, more soluble fragments which are easily lost or displaced from the sea surface (15). The various oxidative modes which lead to more-water-soluble constituents are relatively slow compared to the physical dispersive forces of a wind-driven area. Under calm conditions, after a slick has aged and lost its volatile components, physical, chemical, and biological oxidation will play a more dominant role.

Biological utilization and decomposition of oil at sea is as yet an incomplete and controversial story. A somewhat rosy picture has been portrayed by some investigators who conclude that biodegradation of oil will ultimately decompose a large portion of oil spilled at sea. Bacteria, yeasts, and fungi may oxidize hydrocarbon oils, thereby providing a natural biological cleanup process for beaches and coastal areas. In water with an ample

oxygen supply, microbial oxidation of various petroleum products proceeded at rates of from 0.02 to 0.2 g/m² of oil-covered surface per day in the temperature range 24° to 30°C (16). Microbial attack is most effective against thin films of oil adsorbed at the air/sea interface or on solid particles while being relatively ineffective against massive spills, particularly in the open ocean where oil-oxidizing microorganisms are scarce. Kinney et al. (10) found that biodegradation of crude oil in Cook Inlet, Alaska, is complete in 1 to 2 months. They suggested that methods for sinking or dispersing oil into the water body might be desirable because of the high biodegradability rates at this location.

A less optimistic story emerges when one considers recent reports of extensive quantities of tarlike lumps of oil with varying consistency on beaches and in the open ocean. Horn et al. (17) found such lumps in abundance in the Mediterranean Sea and the eastern North Atlantic Ocean. Some were estimated to be at least 2 months old; others of lesser sea age contained low-boiling fractions which had been trapped in the bulk of the oily mass. Similar observations of oil-tar lumps at sea were reported in a recent study (18) of the North Atlantic Ocean where an average value of 1.0 mg of petroleum tar per square meter of surface water was found. Dennis (19) reported oil in varying degrees of hardness on Florida beaches where incoming oil was present in the surf on 341 out of 355 days of observation. Such information suggests that weathered petroleum products may become quite resistant to decomposition and have long lifetimes in the sea, at its surface, and on its shore.

INFLUENCE OF OIL FILMS ON PROPERTIES OF THE AIR/SEA INTERFACE

The previous sections have considered the spreading, weathering, and distribution of oil with time after its release at the sea surface. The initially fluid petroleum may eventually attain a semisolid condition, either as tarry lumps or as a stable water-in-oil emulsion. Between the initial state of the oil spill and the final, almost refractory state, the oil exists as a thick layer, a thinner iridescent film, and a monomolecular film of surface-active material surrounding the thicker layers. Most existing information on the impact of organic films at the air/sea interface deals with natural sea slicks, which are monomolecular films composed of amphipathic organic molecules. However, extrapolations from thin films to thicker oil layers can be made on the basis of laboratory experiments and field observations of the microscale effects of sea slicks and thin petroleum layers.

Wave Damping

Natural slicks at sea can be seen because a light reflectance anomaly is produced by the capillary-wave damping properties of the otherwise invisible monomolecular film. Simultaneous measurements of wave-damping characteristics and film pressure on freshly collected seawater indicated that the natural adsorbed films damped capillary waves at very low film pressures (20); film pressure is defined as the difference in surface tension between a clean seawater surface and one covered by the organic film. The damping coefficient increased from 0.08 cm⁻¹ for a clean seawater surface to a maximum of about 0.43 cm⁻¹ at a film pressure of 1 dyne/cm using 60-Hz waves (Fig. 2). With a further increase in film pressure,

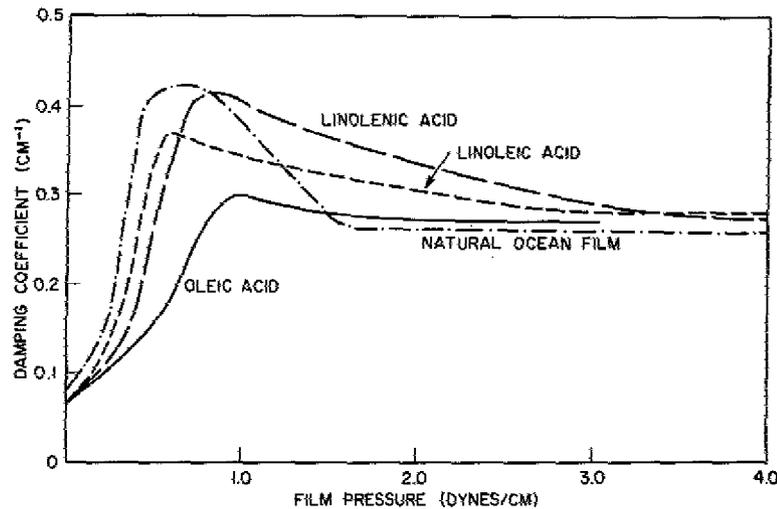


Fig. 2 — Relationship between damping coefficient and film pressure for natural sea surface films, and three fatty acids which are common constituents of such films

the damping coefficient decreased to a value of 0.24 cm^{-1} becoming constant at a 2-dyne/cm film pressure. The damping coefficient k was calculated from

$$a = a_0 e^{-kx},$$

which describes the decay of the linear capillary waves used in the laboratory experiment, where a_0 is the wave amplitude at its source and a is the amplitude at distance x from the source.

Figure 2 is a composite plot of k vs film pressure F for surface films formed from the surface-active compounds in freshly collected seawater and from three pure fatty acids commonly found in sea-surface films. The shapes of these curves reflect the influence of chemically unsaturated fatty compounds (linoleic and linolenic acids) which produce pronounced maxima in k at low F . Furthermore, these data are in accord with the observation that sea slicks can exist at low film pressures and that the surface molecules need not be greatly compressed to damp capillary waves. Since extremely small quantities of surface-active materials at a low state of molecular compression produce easily visible patterns on the sea surface, extensive pollution of the sea surface by oil or other contaminants can be detected readily. However, only in the vicinity of local oil spills or in areas of chronic pollution are such damped conditions prevalent. Thus far the majority of the world ocean surface is capillary active, indicating almost no surface tension reduction and a relatively clean surface condition.

Adsorbed surface-active material not only attenuates existing waves but also inhibits further wave formation (21,22). According to Miles (23), the addition of a sufficient quantity of a soluble surface-active agent (detergent) to produce an immobile film can increase by almost an order of magnitude the minimum wind velocity necessary to produce waves. The monomolecular film surrounding an oil spill and separating windrows of oil will damp and prevent the formation of waves in the capillary regime. In addition, a large areal coverage by the surface film will also decrease the amplitudes of wind-driven

gravity waves by reducing the form drag of the atmosphere on the ocean through the elimination of the waves of shorter wavelength (24).

Capillary-wave attenuation on thicker layers of oil may be determined from

$$k = \frac{8\eta f}{3\gamma}, \quad (3)$$

where f is the ripple frequency, η is the bulk viscosity expressed in poises, and γ is the surface tension of the fluid. Experimental determination of k for pure hexadecane using 60-Hz waves at 25°C gives a value of 0.53 cm⁻¹, a damping coefficient greater than that for seawater covered with a coherent surface film. Furthermore, if we assume values of η and γ for an average crude oil, k is 1.8 cm⁻¹ for 60-Hz capillary waves. Thus, capillary-wave attenuation on a pollutant oil is somewhat greater than that on a monolayer-covered surface and 30 times that on clean seawater at this frequency of wave generation, where $\lambda = 0.52$ cm, a typical capillary wavelength. The low incidence of ripples on the oily surface coupled with its higher viscosity will also diminish wind-driven gravity waves of longer wavelength when the areal coverage of the spill is large. Thus, the uncoupling of air-water interactions by an oil film and its attendant monolayer would produce a calm sea.

Gas Transport

Numerous studies of evaporation retardation by monomolecular films have been reviewed by La Mer (25) and Frenkiel (26). Only those films containing linear molecules capable of close packing are effective in reducing gas transport across the air/water interface. In addition to slowing the evaporation of water, closely packed monolayers can reduce the mass transfer flux of other gases, such as carbon dioxide, methane, nitrogen, and oxygen, by as much as 25 to 40% (27). Films of linear molecules under high film pressure constitute a thin diffusion barrier to the adsorption of oxygen, carbon dioxide, and nitrous oxide by water (28). The diffusion barrier effect is also operative against gas transport from water to air.

In large bodies of water, depletion of oxygen beneath an impermeable surface film is unlikely because dissolved oxygen levels are near or above saturation due to wind-induced mixing (29). Trapped oxygen produced by marine organisms during photosynthetic periods would compensate for any decrease in oxygen uptake through the surface layer. The most important factor which will serve to maintain normal oxygen levels beneath a surface film is the dilation of the surface caused by waves. These surface expansions reduce the close-packed character of the molecules and allow periodic gas exchange. With winds above 15 mph, maintenance of a highly adlineated molecular structure in a surface film is virtually impossible and the film essentially loses all resistance to gas exchange.

A surface film is sometimes mistakenly assumed to interfere with the rate of gas transport to or from the sea. However, only compounds capable of forming rigid films in which the molecules are adlineated and closely packed can retard the evaporation of water. The molecules must be linear in structure so that they may form a close-knit, nonfluid film when forced together under high surface compression (30). The surface-active substances responsible for the spreading and film-forming characteristics of petroleum products contain hydrophilic groups of primarily oxygen, sulfur, or nitrogen. This complex mixture of

compounds includes aromatic, condensed-ring, and branched-chain structures, and cycloparaffin carboxylic acids in addition to the more linear polar molecules. A monolayer formed from such a mixture does not meet the structural requirements of films which retard gas transport. Consequently, the portion of an oil spill which is of monomolecular dimensions should have an inconsequential effect on gas exchange.

However, experiments have shown that a 5-micron duplex film of paraffin oil and a surface-active material may reduce the evaporation rate of water to 15% of that for a clean water surface (31). The efficiency of evaporation inhibition with oil films increases with wind velocity (32), and it was concluded that the effect was due to the diffusional resistance of the oil and its interfacially oriented film rather than the resistance of the stagnant diffusion-controlled air layer above the oil. Above a film thickness of 10 microns the evaporation resistance increased with film thickness and depended on the nature of the spreading agent in the oil. Under nonturbulent air flows, films thicker than 50 microns decreased evaporation rates to less than 1% of that for clean water. Powell (33) investigated the influence of oxidized oil films up to 2.5 cm in thickness on the evaporation of water and determined that a maximum retardation occurred between a 0.6- and 1.0-cm film thickness. At greater oil-film thicknesses the efficiency of evaporation retardation decreased. This latter result was attributed to convective effects in the thicker films which overcame the diffusion barrier effect. The lower rate of diffusion of water through oil as opposed to that in air accounts for the evaporation retardation; the diffusion coefficient for water is about 10^4 greater in air than in oils (33). It was observed that under the influence of wind a uniform oil film was difficult to maintain in the micron range. These surface films broke up into lenses which were in equilibrium with their supporting monomolecular films, a factor to be considered for any oil spill. In such instances, wind-wave effects break continuous films into discontinuous puddles of oil surrounded by thin films and monolayers.

In addition to inhibiting the exchange rate of water across the air/sea boundary, oil layers will slow exchange of other gases. In the case of oxygen, the effect is due to slowed diffusion processes and to the uptake of oxygen by the oil through autooxidative reactions. However, it is unlikely that oxygen depletion would reach disastrous proportions near the sea surface unless the oil spill uniformly covers a vast area. Uniform coverage is rare because of wave-induced dilations which thin the film, drive it into windrows, and consequently create open sea surface areas for gas exchange. Furthermore, horizontal transfer beneath the slick from saturated water masses can resupply oxygen-deficient zones. Only in small bodies of water with little mixing should oil films cause abnormal oxygen levels. Of course, this relatively clean bill of health with regard to oxygen depletion at sea relates to effects at the sea surface only. If large quantities of petroleum products are submerged into the bulk water, the biological and chemical oxygen utilization which will result could create a situation critical to marine life.

Exchange of Solids and Liquids

The transfer of solids and liquids from sea to air is effected by sea spray and bursting bubbles. These processes are modified by organic films, oil layers, and emulsions at the air/sea boundary. Free gas bubbles may be produced in the sea by the decomposition of detrital matter, the impact of raindrops, and the breaking of waves. By scavenging surface-active material and foam-stabilizing particulate substances, bubbles promote the formation of foams. In addition, bursting air bubbles generate salt-containing aerosols by disintegrating

the thin film of water which separates the air in the bubble from the atmosphere (34). When surface films are present, fragments from bursting bubbles transfer its organic components into the marine atmosphere (11). In fact, the ejected portions of the bubble crown (film drops) and the jet drops produced by collapse of the bubble cavity may remove any sea-surface matter — animal, vegetable, or mineral. Oil films are readily stripped from the water surface by this process.

The longevity of air bubbles and foam at the air/water interface depends on both the surface activity of the seawater and the physical nature of sea-surface films (35). In the absence of a surface film, the lifetime of a bubble is determined by the surface-active material adsorbed during its passage upward through the ocean. The existence of a sea slick with monomolecular dimensions at the point of bubble emergence will significantly reduce bubble stability and the slick will act as an antifoaming agent even though the bulk seawater may be rich in foam-stabilizing substances. Similar circumstances prevail for oil films up to 1000 Å thickness as indicated by recent data from this laboratory presented in Fig. 3. Bubble lifetimes (58 sec average value) were first measured at the surface of freshly collected seawater contained in a glass hydrophil tray. Single bubble duration was then measured as a function of the film pressure of a crude oil film spread onto the seawater substrate from a dilute CHCl_3 solution. The oil layer which was initially of monomolecular dimensions was compressed in stages, and bubble lifetime and film pressure were measured at each film area. Before compression of the oil film was initiated, the bubbles were stable since they were influenced by soluble surface-active material which they had collected by adsorption on their rise to the surface. This stability was due to the rapid repair of the protective surface film by the available supply of foam-stabilizing compounds from the bulk seawater. By compressing the oil film, bubble lifetime decreased substantially to values of zero at high film pressures where the oil film behaved like a brittle, solid sheet, and the air bubbles burst instantaneously on reaching the surface. The

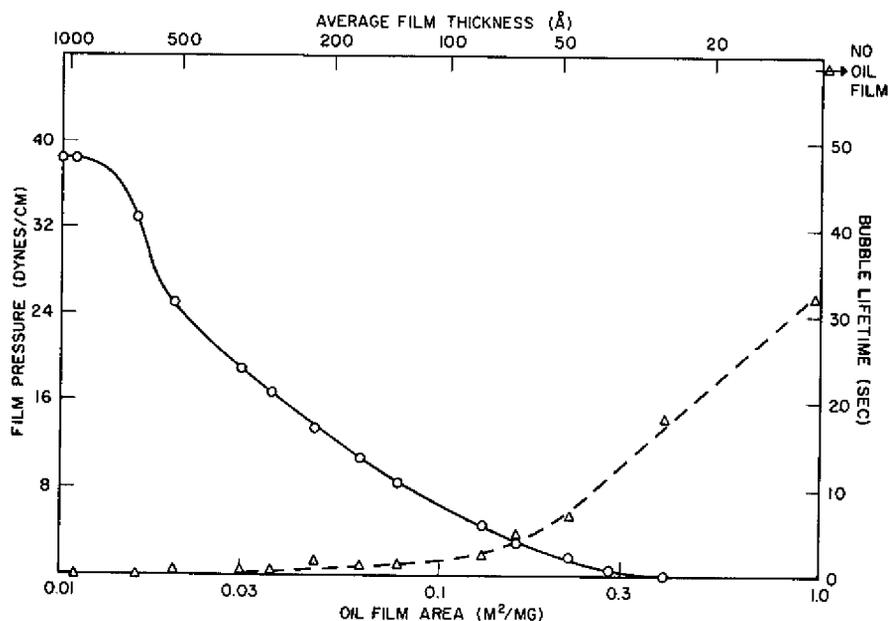


Fig. 3 — Bubble lifetime (dashed line) and film pressure (solid line) vs thickness of a spread film of crude oil

compressed, water-insoluble oil film then became the controlling factor in determining bubble duration and foam stability. Especially at high film pressure there was an increased instability in the embrittled film, and the probability of film rupture was large.

Conversely, we have observed that somewhat thicker oil films have an opposite effect when they are as thick as the diameter of the air bubble. The millimeter-thick multilayers of oil appear to contain sufficient foam-enhancing, surface-active material to stabilize clusters of bubbles at the air/oil interface. Although it has not been demonstrated through experiment, the monolayer-covered area surrounding an oil slick may well form rigid films which decrease foam lifetime since they will be composed primarily of water-insoluble constituents. However, the thicker multilayers of oil will contain sufficient foam-stabilizing, surface-active material to perpetuate bubble clusters and water-in-oil emulsions.

The foaming characteristics of the sea surface determine the rate of transfer of liquids and solids via breaking air bubbles. The addition of water-insoluble surface films to bubbled seawater increased the concentration of bubble-generated salt nuclei by as much as threefold (36). No increases in nuclei concentration resulted when these films were spread onto the surface of clean aqueous systems which did not contain surface-active, foam-forming materials. Consequently, the increased salt nuclei concentration resulted from a modification of the bubble-bursting process by the surface film. The water-insoluble film decreased the degree of foaming at the seawater surface and enhanced the immediate breaking of bubbles. Thus, there was a greater rate of fragmentation of the air/water interface which increased the concentration of bubble-generated salt particles over that produced from a foamy surface. However, it is to be expected that a thick oil film not only will decrease the production of bubbles and spray by inhibiting breaking water but also will retard bubble bursting through stable emulsion formation. Thus, a thick oil layer will cause a decreased rate of transport of matter from sea to air while thinner oil films in the micrometer range and monomolecular layers should increase transport rates for identical bubble-bursting and sea-spray situations.

In addition to damping physical processes at the air/sea interface, an oil spill may also affect the physics of the marine atmosphere. Bubbles which burst at an oil-covered surface eject water drops coated with an oil layer which retards drop evaporation (12). The evaporation rates of distilled water drops and drops coated with 1-hexadecanol and various pollutant oils are compared in Fig. 4. Oil-coated drops were produced by the rupture of 2-mm air bubbles at a water surface covered by a 10-micron-thick oil film. The evaporation rates, expressed as $-2r \, dr/dt$, where r is the radius of a waterdrop, were up to 25 times larger for distilled water than for the oily drops. It is interesting to note that the evaporation rate for the oil-coated drops was sometimes less than that for the drops whose surface was covered with a monomolecular film of 1-hexadecanol, an effective agent for the retardation of evaporation. Under windy conditions at sea, considerable oil would be transferred into the marine atmosphere where it could retard droplet evaporation and perpetuate an oily mist.

The movement of matter from the atmosphere into the bulk ocean is also impeded by slicks and oil spills. Lipophilic aerosol fallout from the atmosphere (e.g., chlorinated hydrocarbon) can be concentrated in sea slicks (37). The concentration effect is due to the preferential solubility of the very-water-insoluble pesticides in nonpolar liquids and surface films. For example, the partition coefficient of *p, p'*-DDT between sedimental river oils and water is 1.45×10^6 according to Hartung and Klinger (38), who found a concentrating effect by such oils on DDT in the Detroit River. Chlorinated hydrocarbon

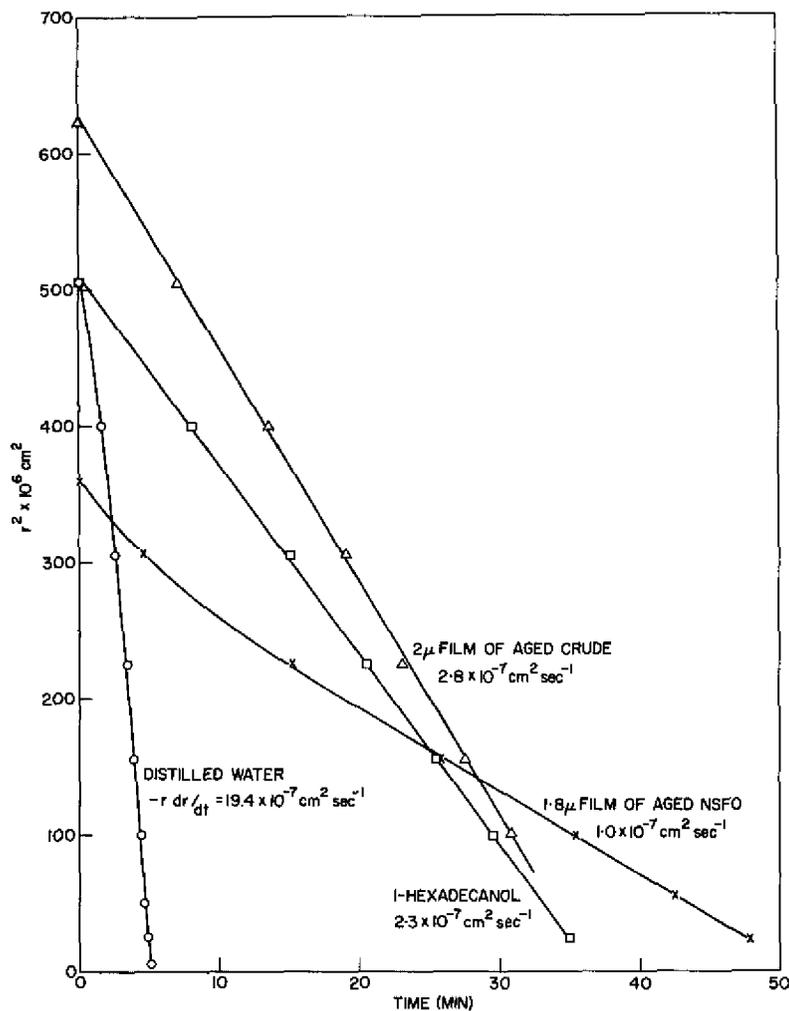


Fig. 4 — Evaporation characteristics of uncoated distilled water drops and drops coated with 1-hexadecanol or oil films at $25^\circ \pm 0.2^\circ \text{C}$ and $50 \pm 2\%$ relative humidity

fallout will be concentrated first in oil spills, then distributed into the sea by the various natural dispersive forces acting on the oil film. These persistent organic pollutants may then be further concentrated and incorporated into the ocean's food web through biological assimilation.

EXTENT OF OIL IN THE OCEANS AND ON ITS SURFACE

A first approximation to the extent of oil pollution of the seas can be obtained from the solution of two problems. The input of oil from ships, oil production operations, accidental spills, and river discharges for 1969 is estimated to be 2.08×10^6 metric tons (39). This figure does not include atmospheric fallout of petroleum products onto the sea, which is estimated to be five times greater than the fluid input (39). Dividing the volume of the world ocean, 1.4×10^{21} l, into 2.08×10^{15} mg of oil, we obtain an

average input concentration rate of about 1.5×10^{-6} mg/l per year if the oil is assumed to be uniformly distributed throughout the oceans. This value is small when compared to the average dissolved organic content of seawater of 0.5 to 1.0 mg/l (40). Of course, this comparison is subject to many qualifications since most petroleum products are entering the seas in specific areas of the Northern Hemisphere and in small localized areas when accidentally spilled. The oil is not uniformly distributed but tends to be concentrated at surfaces or in ocean sediments. Furthermore, a local spill of large proportions can produce significant effects on the marine environment since its concentration would far exceed the natural organic level for a period of time in the vicinity of the injection point.

The second problem deals with the concern that the ocean surface may become covered with an oil film whose influence on air-sea interactions could cause environmental alterations on a global scale. The annual oil input may be expressed as 2.08×10^{12} cm³ if an oil density of 1 is assumed. Dividing by 3.6×10^{18} cm², the surface area of the seas, we obtain 5.8×10^{-7} cm or 58 Å for the thickness of this quantity of oil spread uniformly onto the ocean's surface. This figure is about double the thickness of a monomolecular layer, indicating that the annual oil loading would be sufficient to paint the sea with a film composed of hydrocarbons and surface-active material. Again, however, the results of the calculation are misleading for many obvious reasons. The chemical, physical, and biological factors which disperse surface films into air and water and modify its character (Fig. 1) would remove much of the film and prevent it from forming an intact ubiquitous layer. The end product of weathered oil on the sea surface appears to be floating lumps of tarlike petroleum or stable water-in-oil emulsions. Most of the film-forming constituents have been lost from the surface or are contained within the weathered petroleum products so that they do not contact the water surface and no further spreading occurs.

The concentration of surface-active molecules in a large portion of the sea surface must still be less than 0.57 mg/m². This value is the minimum concentration of oleic acid required to initiate capillary-wave damping. Since most of the sea surface is covered with capillary waves when the wind is blowing and slicks of any kind are rare away from coastal areas, it appears that the likelihood of a worldwide sea slick is remote at present. Capillary-wave damping by surface films provides a sensitive indicator of the onset of serious surface contamination.

We still do not know how much organic pollution the seas can accept before they become burdened to the extent that climatic, ecological, and other natural imbalances result. Certainly, local overloadings are occurring with increasing frequency, and damage to marine life, recreational facilities, the fishing industry, and the esthetics of the coastal zones have resulted. A disturbing case in point is the Viareggio phenomenon occurring along the west coast of Italy adjacent to the Ligurian Sea, a portion of the Mediterranean (41). Industrial and municipal organic pollutants pouring into the sea from nearby rivers produce vast areas of film-covered coastal water. Onshore winds carry petroleum and surface-active constituents of this film inland where they are coating the needles of coastal pine trees. Serious interference with transpiration results, and vast numbers of trees are dead or dying. This phenomenon is directly related to sea-surface pollution and certainly presages further disasters along coastal areas affected by industrial and urbanized regions.

SUMMARY AND CONCLUSIONS

Once released onto the sea, oil spreads rapidly under the influence of wind, surface currents, and hydrostatic forces. Eventually the oil layer thins and attains crude equilibrium with thin films which contain large quantities of surface-active constituents. Surface forces then govern additional spreading. The time to reach this condition depends on the spill volume, the meteorological conditions, and the character of the oil. Several natural forces operate on the slick to disperse its constituents, partly into the marine atmosphere but largely into the sea. The relative influence of the various dispersive forces changes as the oil ages and spreads. Weathering, dispersion, and air-sea dynamics ultimately degrade the spill to tarlike lumps and/or stable water-in-oil emulsions with long and as yet undetermined lifetimes at the sea surface.

Layers of oil and their attendant monomolecular films influence various properties of the air/sea interface and modify exchange processes between the atmosphere and the ocean. Small waves are resisted and attenuated, and the interaction between wind and waves is uncoupled through elimination of form drag. Gas exchange is inhibited by the films of oil, but not to a serious extent in the open ocean. Liquid and solid exchange is altered, organic fallout is concentrated at the surface by the oil, and oil is transported into the marine atmosphere where it may influence atmospheric processes. In general, the conclusion drawn is that a large sea slick or oil film damps its environment by replacing a high-surface-tension, dynamic water surface with a more phlegmatic, less mobile, organic/air interface.

Although the ratio of contaminant to natural film-forming material in the sea is increasing, the natural oceanic background of organic matter is still large in comparison to the man-made input. However, spills of oil, river inputs, or ocean dumping can create localized conditions where the resulting surface films are predominantly a result of human activity. Severe damage to the marine environment occurs in these areas affected by man. Although a worldwide ocean surface film is unlikely in the near future, weathered lumps of petroleum products and chemical scums floating on and near the water surface will increase if biological degradation and physical dispersion do not keep pace with the world loading of these contaminants. Should a ubiquitous film one day cover the seas, there would be sensible modifications to the marine environment although the magnitude of such alterations is difficult to predict at the present time.

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