FATE OF SPILLED OIL IN MARINE WATERS:
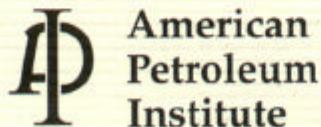
WHERE DOES IT GO?

WHAT DOES IT DO?

HOW DO DISPERSANTS AFFECT IT?

AN INFORMATION BOOKLET FOR DECISION-MAKERS

American
Petroleum
Institute

STEP
*Strategies for Today's
Environmental Partnership*

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American Petroleum Institute
Environmental, Health, and Safety Mission
and Guiding Principles

MISSION

The members of the American Petroleum Institute are dedicated to continuous efforts to improve the compatibility of our operations with the environment while economically developing energy resources and supplying high quality products and services to consumers. We recognize our responsibility to work with the public, the government, and others to develop and to use natural resources in an environmentally sound manner while protecting the health and safety of our employees and the public. To meet these responsibilities, API members pledge to manage our businesses according to the following principles using sound science to prioritize risks and to implement cost-effective management practices:

PRINCIPLES

- To recognize and to respond to community concerns about our raw materials, products and operations.

- To operate our plants and facilities, and to handle our raw materials and products in a manner that protects the environment, and the safety and health of our employees and the public.

- To make safety, health and environmental considerations a priority in our planning, and our development of new products and processes.

- To advise promptly, appropriate officials, employees, customers and the public of information on significant industry-related safety, health and environmental hazards, and to recommend protective measures.

- To counsel customers, transporters and others in the safe use, transportation and disposal of our raw materials, products and waste materials.

- To economically develop and produce natural resources and to conserve those resources by using energy efficiently.

- To extend knowledge by conducting or supporting research on the safety, health and environmental effects of our raw materials, products, processes and waste materials.

- To commit to reduce overall emission and waste generation.

- To work with others to resolve problems created by handling and disposal of hazardous substances from our operations.

- To participate with government and others in creating responsible laws, regulations and standards to safeguard the community, workplace and environment.

- To promote these principles and practices by sharing experiences and offering assistance to others who produce, handle, use, transport or dispose of similar raw materials, petroleum products and wastes.

FOREWORD

API PUBLICATIONS NECESSARILY ADDRESS PROBLEMS OF A GENERAL NATURE. WITH RESPECT TO PARTICULAR CIRCUMSTANCES, LOCAL, STATE, AND FEDERAL LAWS AND REGULATIONS SHOULD BE REVIEWED.

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ACKNOWLEDGMENTS

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BACKGROUND ON THIS BOOKLET SERIES

Beginning in 1994, the Marine Spill Response Corporation (MSRC), and later the Marine Preservation Association (MPA), sponsored a study to examine the reasons for the apparent differences between the science of dispersant use and perceptions of ecological effects. Using a prescribed risk communication methodology, this study compared the mental models (an individual's thought processes in making a decision regarding a particular issue) of US dispersant decision-makers and other stakeholders to an expert model (expert consensus of the relevant decision concepts that might be used), specifically looking at spilled oil in comparison to chemically-dispersed oil. Through a series of interviews and written questionnaires, a number of dispersant misperceptions were identified. These misperceptions were translated into topics for booklets that would provide dispersant information in a concise and reader-friendly format. For more information on the MSRC/MPA study, please see Bostrom *et al.*, 1995, Bostrom *et al.*, 1997, and Pond *et al.*, 1997a.

As a result of the MSRC/MPA work, in 1996, the American Petroleum Institute (API) commissioned the preparation of three of the dispersant booklets:

- Fate of Spilled Oil in Marine Waters: Where Does It Go? What Does It Do? and How Do Dispersants Affect It?

- A Decision-maker's Guide to Dispersants: A Review of the Theory and Operational Requirements.

- Defining the Links Between Fate and Transport Processes with Exposure and Effects of Oil and Chemically Dispersed Oil in the Environment.

This booklet is the first in the series.

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OVERVIEW

- The American Petroleum Institute commissioned the preparation of three booklets to help bridge the gap in the understanding of dispersant use, effectiveness, and effects.

- This first booklet focuses on oil chemistry and oil weathering, two concepts that spill response decision-makers need to interpret dispersant information more effectively. This booklet then presents information on how dispersants alter or affect the weathering process

- Oils are typically described in terms of physical properties, used to determine, in part, how an oil spilled on water will react under various ambient conditions:

  ⇒ <u>Specific gravity</u> – ratio of the mass of a given material to the mass of fresh water For most crude oils and refined products, specific gravity is usually between 0.78 and 1.0.

  ⇒ <u>API gravity</u> – scale for measuring fluid specific gravities based on an inverse relationship with specific gravity. For instance, an oil with a low specific gravity (0 73) will have a high API gravity (62). This scale was developed so that larger values are used.

  ⇒ <u>Pour point</u> – the temperature below which oil will not flow.

  ⇒ <u>Viscosity</u> – an oil's internal resistance to flow. A highly viscous oil will not flow easily.

  ⇒ <u>Asphaltene and wax content</u> – non-hydrocarbon portions of the oil which are defined in terms of solubility. An oil with a high asphaltene and wax content is generally heavier.

  ⇒ <u>Trace constituent content</u> – these include nickel, vanadium, iron, aluminum, sodium, calcium, and copper. Oils with large concentrations of these trace constituents tend to emulsify easily.

- Oil is a complex mixture of thousands of different compounds, composed primarily of carbon, hydrogen, sulfur, nitrogen, and oxygen. Hydrocarbons (composed solely from carbon and hydrogen atoms) are the most abundant compounds found in crude oils

- After oil is discharged into the environment, a wide variety of physical, chemical, and biological processes begins to transform the discharged oil Collectively called "weathering," the rate and significance of these processes are dependent on the type of oil spilled, spill location, and weather conditions at the time of the spill.

- Ten weathering processes are discussed:

  ⇒ <u>Spreading and advection</u> – spreading is the movement of the entire slick horizontally on the surface of the water due to effects of gravity, friction, viscosity, and surface tension. Advection is the movement of the oil due to the influence of overlying winds and/or underlying currents. Neither is uniform, and large variations in oil thickness occur within the slick. Spreading dominates the initial stages of a spill and involves the whole oil, that is, it does not partition the various components of the oil or affect its chemical composition. Spreading and advection continue for approximately one week to ten days following the discharge, or until the oil is contained by shorelines, collection efforts, or other obstructions.

⇒ <u>Evaporation</u> – the preferential transfer of light- and medium-weight components of the oil from the liquid phase to the vapor phase. It is the primary weathering process involved in the natural removal of oil from the sea surface. During the first 24 to 48 hours of the spill, it is the single most important weathering process, from the standpoint of volume reduction. Evaporation starts immediately following the spill and continues for approximately two weeks.

⇒ <u>Dissolution</u> – the transfer of oil components from a slick on the surface into solution in the water column. It is a relatively insignificant weathering process in terms of reducing the volume of the spills and typically occurs within the first 24 hours of a spill.

⇒ <u>Natural dispersion</u> – the process of forming small oil droplets that become incorporated into the water column in the form of a dilute oil-in-water suspension. Dispersion reduces the volume of the slick at the surface but does not change the physiochemical properties of the oil. Following evaporation, it is the most important process in the breakup and disappearance of a slick. It begins soon after the spill occurs and reaches a maximum rate in approximately 10 hours following a spill.

⇒ <u>Emulsification</u> – the mixing of water droplets into oil spilled on the water's surface. Water-in-oil emulsions are highly viscous and have densities approaching seawater. Once the oil has emulsified, the weathering of oil can be significantly reduced. Emulsification begins during the first day of the spill and can continue to occur throughout the first year. The largest volume of emulsions is typically formed within the first week of the spill.

⇒ <u>Photo-oxidation</u> – sunlight, in the presence of oxygen, transforms hydrocarbons through photo-oxygenation into new by-products. It occurs at the very surface of the oil and directly on components which have physically separated from the whole oil. It plays a fairly minor role in the overall weathering of the oil, and can last for several weeks to a month following a spill.

⇒ <u>Sedimentation and shoreline stranding</u> – sedimentation is the incorporation of oil within both suspended and bottom sediments. Sedimentation is a very important process in shallow, rough sea conditions where bottom sediments are repeatedly resuspended. It begins soon after the spill occurs and peaks several weeks into the spill. Shoreline stranding is the visible accumulation of oil on shorelines following a spill. It is affected by the proximity of the spill to the shore, intensity of current and wave action on the affected shoreline, and the persistence of the spilled product.

⇒ <u>Biodegradation</u> – process where naturally occurring bacteria and fungi consume hydrocarbons to use as a food source. Carbon dioxide and water are excreted as waste products. It is a significant but slow process. It begins several days following a spill and will continue as long as hydrocarbons persist.

- These weathering processes occur simultaneously with each other, as they overlap through the course of a spill. The processes interact and affect each other and in turn affect the properties of the spilled oil.

- Dispersants are chemicals composed of surface-active agents (surfactants), solvents, and stabilizing agents. The surfactants in the dispersants reduce the interfacial tension at the water:oil interface and promote the break-up of the slick into fine droplets, facilitating the dispersion of the oil into the water column. They also act to prevent the recoalescence of suspended, chemically dispersed oil droplets.

- Dispersants affect natural weathering processes in the following ways (please note these are generalities):

    ⇒ <u>Spreading</u> is enhanced.

    ⇒ <u>Evaporation</u> will primarily occur as a secondary weathering process following dispersant application.

    ⇒ <u>Natural dissolution</u> will probably be increased.

    ⇒ <u>Natural dispersion</u> will probably be enhanced.

    ⇒ <u>Emulsification</u> will decrease.

    ⇒ <u>Photo-oxidation</u> will probably be slowed.

    ⇒ <u>Sedimentation</u> and shoreline stranding is reduced.

    ⇒ <u>Biodegradation</u> is enhanced.

Section 1: Introduction

Consider this scenario...an oil tanker has had an offshore accident and is releasing its cargo. It is your job to recommend response options to protect the sensitive nearshore environment. One of the response options you are considering is chemical dispersants. Although you have worked on oil spills in the past, dealing with these spills is only one facet of your job which has wide-ranging responsibilities. You want to have a good understanding of what happens to the oil when it is spilled and how dispersants can change that, but you may not be a biologist or chemist by training, and much of the information you have available is very technical.

This scenario is all too common. As a decision-maker involved in oil spill response, you have received extensive on-the-job training, but you don't live and breathe oil spills and don't use your oil spill training every day. Consequently, much of the literature and information available to assist you during planning and actual response operations is too technical, too long, and does not help resolve your questions and concerns. You need short summary reports which accurately but concisely provide the answers you need to help make a decision regarding the use of dispersants during an oil spill. This booklet, the first in a series of three, helps fill that need.

Purpose of Booklet

This booklet was developed for oil spill response decision-makers. It summarizes what happens to oil that spills on marine waters. To make informed decisions on using dispersants, or any countermeasure, it is important first to have a clear understanding of the overall fate of the oil entering the environment: What will the oil do once it is spilled? Where will it go? Once the fate of the oil alone is understood, we can then examine how the addition of dispersants will affect that fate.

All of these answers are found in this booklet, in an easy-to-read format supplemented with diagrams and figures. Each fate process involved is reviewed independently, including a discussion of how significant the process is, when it occurs following a release, and what properties or ambient conditions influence it. The booklet then presents information on how dispersants affect or alter the various fate processes.

This booklet is also designed to identify and explain unfamiliar terms associated with oil that may be used by technical experts during planning or response operations. The first time a new technical term is used

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within this booklet, it will appear in an ALL CAPS format; this signifies that a more detailed explanation or definition is present in the right or left narrow margin at or near where the word(s) is first used within the main text.

SECTION II: OIL CHEMISTRY REVIEW

An oil's physical properties and chemical composition are important factors that influence fate processes.

PHYSICAL PROPERTIES OF OIL

Oils are typically described in terms of their physical properties [e.g., SPECIFIC GRAVITY and API GRAVITY, POUR POINT, VISCOSITY, ASPHALTENE and WAX CONTENT, and the presence of TRACE CONSTITUENTS (Payne, 1994)]. These parameters (combined with various environmental information, e.g., wave height, wind speed, currents, etc.) are used to determine how oil spilled on water will react under ambient conditions.

DENSITY

The density of oil relative to fresh water is typically expressed in terms of specific gravity or API gravity. Density can help the decision-maker determine if an oil is likely to sink or float in the water column following a discharge.

Specific Gravity

Specific gravity is defined as the ratio of the mass of a given material (e.g., oil) to the mass of freshwater, for the same volume and at the same temperature. Clark and Brown (1979) determined that the majority of crude oils and refined products have specific gravity values (SG) between 0.78 and 1.00. As these values are less than the SG for fresh water (1.0 at 4°C), they will float on the water surface.

Weathering is the combination of physical and chemical changes in oil composition. It may result in the removal of oil from the water's surface to the atmosphere, water column, sediments, and shorelines.

Most oils and refined products have a specific gravity of less than 1.0; oils with a specific gravity greater than 1.0 tend to sink or be neutrally buoyant (neither sink nor float on top, but stay as a unit within the water column). When these products are released onto the water, they typically float unless they gather sediment, undergo additional WEATHERING, or are consumed by various marine animals. The specific gravity of most crude oils and refined products lies between 0.78 and 1.00 (Table 1) (Overstreet and Galt, 1995). As an oil or refined product weathers (components are lost to the environment), the specific gravity of that oil will increase. With an oil that has a specific gravity near 1.00 (in freshwater) or 1.03 (in saltwater), weathering may result in the oil having a specific gravity value greater than or equal to the surrounding water. The weathered oil may sink or it may become neutrally buoyant (Scholz *et al.*, 1994).

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Product	Specific Gravity	API Gravity	Pour Point (°F)	Boiling Point Range (°F)	Viscosity cSt @ 68 °F	Relative Persistence
Gasoline	0.74 to 0.73	59 to 62	NA	104 to 302	~0.5	1
Jet Fuel (JP-4)	0.75 to 0.80	44.3 to 56.7	NA	203 to 518	0.94	~2
Kerosene	0.80 to 0.88	43 to 29	0	392 to 572	2.0 to 3.5	NA
Fuel Oil No. 2 (Diesel)	0.88	29	20	93 to 365	2.25 to 5.0	8
Lube Oil (crankcase)	0.87	29	-35	710 to 822	79 to 86	~55
Kuwait Light Crude Oil	0.83	37.8	-50	NA	13.8	~320
Fuel Oil No. 6 (Bunker)	0.96 to 0.97	10 to 17.5	60	615 to 826	>500	400
North Slope Crude Oil	0.89	17.5 to 35	-	NA	58.4	~450
San Ardo (CA) Crude Oil	0.99	5 to 17.5	80	NA	4754	~590
Residual Asphaltene	-	<10	-	>752	-	1600

Table 1. A comparison of oil properties for a variety of crude oil and refined oil products. All numbered persistence data are based on the relative persistence of the product in the environment, divided by the least persistent oil product (gasoline). Adapted from Curl and O'Donnel (1977), Gilfillan (1993), API (1990), and Markarian et al., (1993).

API Gravity

This scale (ranging from essentially 0 to more than 60; Table 1) can provide insight as to the type of oil spilled and how it will generally react in the environment. In general, the larger the API gravity value, the greater amount of light-weight components an oil or refined product has (Figure 1). With decreasing API gravity values (less than 17.5), which means increasing the amount of medium and heavy-weight components, the oil or refined product is likely to remain in the system. As an oil or refined product weathers (components are lost to the environment), the API gravity of that oil will decrease. With an oil that has an API gravity at or near 10, additional weathering may result in the oil having an API gravity value less than or equal to the surrounding water. The weathered oil may sink, or it may become neutrally buoyant (neither sink nor float on top, but stay as a unit within the water column) (Scholz et al., 1994).

POUR POINT

If the temperature of the water is as cold or colder than the oil's pour point, the oil will stiffen up and no longer flow. In cold climates and cold waters, many of the heavy refined products which have high temperature pour points must be heated during transport and pumping. When these types of oils are spilled into the water, they will not flow readily or

API gravity is a scale for measuring fluid specific gravities based on an inverse relationship with specific gravity. This scale was primarily developed to expand the scale for specific gravity so that larger values are used. An oil with a low specific gravity (e.g., gasoline; SG = 0.73) will have a high API gravity (°API = 62); inversely, an oil with a high specific gravity (e.g., very heavy crudes; SG = 0.98) will have a low API gravity value (°API = 13).

API gravity = (141.5 / SG *) - 131.5

* at 60 °F

Pour point is the temperature below which oil will not flow.

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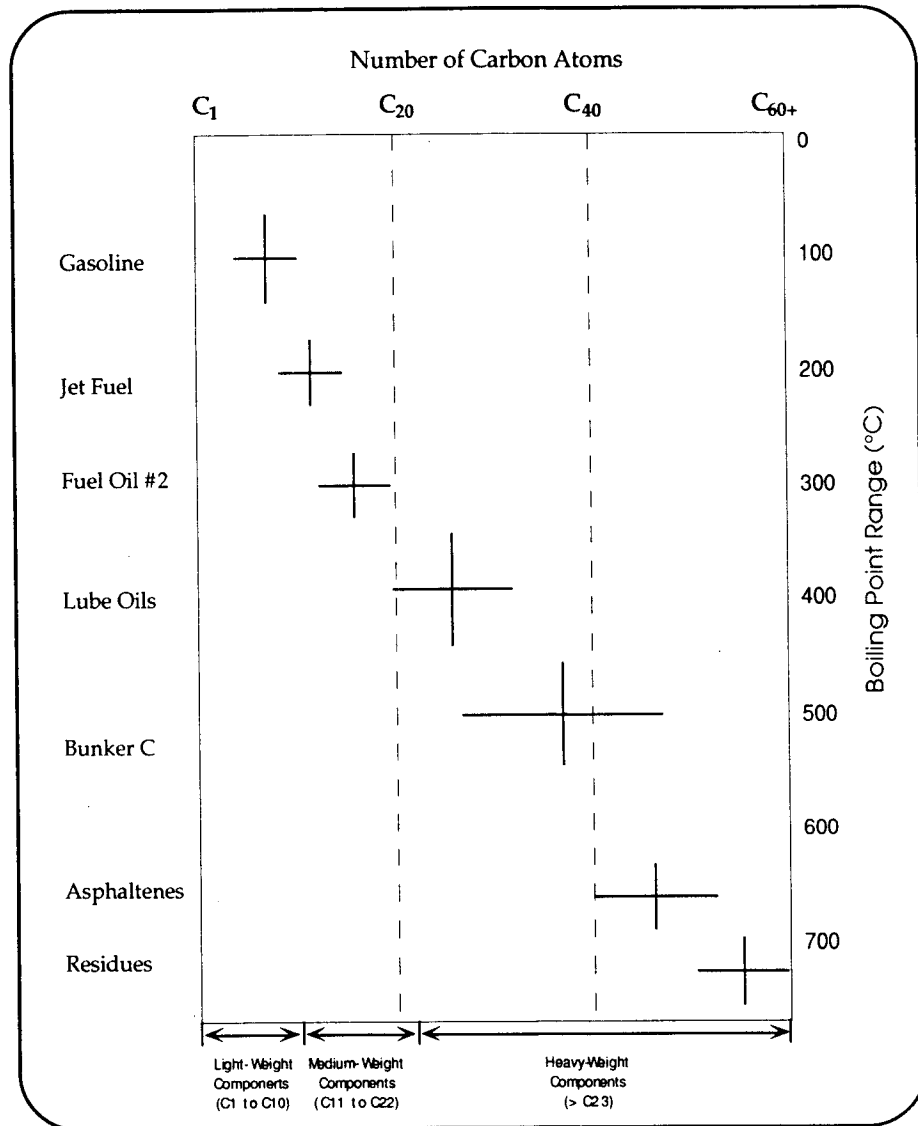
Figure 1. Distribution of various refined petroleum products as developed from a "generic" crude oil. No concentration data are provided because the exact composition of the oil product will vary due to the source and refinery. Adapted from Markarian *et al.*, (1993).

Viscosity *is an oil's internal resistance to flow. A highly viscous oil will not flow easily. This physical property of the oil or refined product is important to understand as it helps determine the oil's behavior during a spill.*

Centistoke *(cSt) is a unit of measurement used in defining the KINEMATIC VISCOSITY of a fluid. cSt = 1/100 St.*

Kinematic viscosity *is a unit of measurement used to define an alternative viscosity measurement. This alternative viscosity measurement is simply the fluid's dynamic viscosity divided by its density. Measured in St or stoke.*

spread. In these instances, the oil can move "like semi-submerged strands of thick rope or 'icebergs'; the majority of the bulk oil resid[ing] just below the water surface" (Lewis and Aurand, 1997). For refined oil products, pour point values can vary between -60 °C for jet fuels to +46°C for waxy No. 6 fuel oils (Overstreet and Galt, 1995).

VISCOSITY

Viscosity is measured in CENTISTOKEs (cSt). An oil's viscosity influences or controls the success of cleanup operations, since very viscous oils are difficult to recover with conventional technologies (e.g., disc skimmers) (Overstreet and Galt, 1995). As oil spilled on the water un-

dergoes weathering processes, the natural viscosity of the oil increases with the loss of many of its components.

ASPHALTENE AND WAX CONTENT

Asphaltenes and waxes are non-hydrocarbon portions of the oil which are defined in terms of their solubilities, rather than their compositions. Oils and refined products with high asphaltene content are typically heavier, more persistent oils. Waxes are also heavy-weight components of the oil that are in crystal form when the oil is below its pour point (Payne, 1994). These components in the oil do not undergo any significant weathering alterations (Lewis and Aurand, 1997; Payne, 1994) and are essentially considered inert RESIDUE.

TRACE CONSTITUENT CONTENT

Trace chemicals in an oil's makeup, such as nickel, vanadium, iron, aluminum, sodium, calcium, copper, and others can also be important in stabilizing emulsions and affecting weathering (NRC, 1985; Payne, 1994). Oils with large concentrations of these trace constituents tend to emulsify readily.

OIL COMPOSITION

Oil is not one compound or chemical, rather it is a complex mixture of thousands of different compounds (Lewis and Aurand, 1997); there are also many types of crude oils. Because each oil field was formed millions of years ago from different components, crude oils can "vary in consistency from clear straw-colored liquids to viscous black semi-fluids with the consistency of ice cream" (Gilfillan, 1993). In fact, Neff (1990) reports that crude oils drawn from different wells in the same region can have markedly different properites, and even the properties of oil taken from an individual well can vary with the depth of the well and year of production.

Crude oils are composed primarily of five elements: carbon, hydrogen, sulfur, nitrogen, and oxyen. These five elements are present in various combinations within the oil. Hydrocarbons (composed solely from carbon and hydrogen atoms) are the most abundant compounds found in crude oils, up to 85 percent of the overall mixture (Gilfillan, 1993) (Table 2). Refined products such as gasoline and fuel oil No. 6 (bunker fuels) are produced by separating (through a distillation process) the crude oil into a number of "CUTS" with specific BOILING POINT RANGEs. The three most valuable refinery products are typically gasoline, jet fuels, and fuel oil No. 2 (home heating oil and diesel fuels) (Gilfillan, 1993).

Table 2. Percentages of the various components of a "generic" oil. Adapted from Helton (1996).

Element	Weight %
Carbon (C)	82 to 87
Hydrogen (H)	11 to 15
Sulfur (S)	0 to 8
Nitrogen (N)	0 to 1
Oxygen (O)	0 to 0.5

Because of our extensive use of crude oil and refined products, the potential exists for accidental releases into the environment. In order to assess environmental impacts from spilled oil, and for ease of identification, the hydrocarbons contained in crude and refined oils are often categorized into four basic classes of petroleum hydrocarbons based on molecular composition: alkanes, naphthenes, aromatics, and alkenes (taken from Helton, 1996).

Alkanes $C_nH_{(2n+2)}$
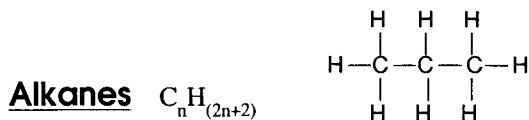
Also called normal paraffins, alkanes are characterized by branched or unbranched chains of carbon atoms with attached hydrogen atoms and contain only single carbon-carbon bonds (no double or triple bonds between carbon atoms).

Naphthenes C_nH_{2n}
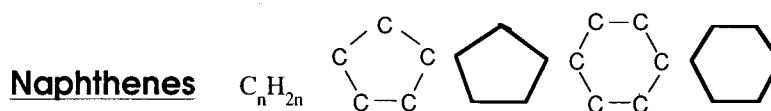
Also called cycloalkanes or cycloparaffins, naphthenes typically comprise about 50 percent of the average crude oil. Naphthenes are similar to alkanes, but are characterized by the presence of simple closed rings of carbon atoms. Naphthenes are generally stable and relatively insoluble in water.

Aromatics 6 carbon ring(s)
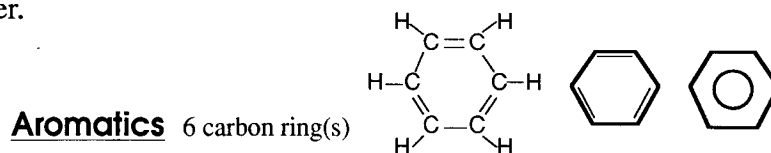
Aromatics are a class of hydrocarbons characterized by rings with six carbon atoms. Aromatics are considered to be the most acutely TOXIC component of crude oil, and are also associated with chronic and carcinogenic effects. Many low-weight aromatics are also soluble in water, increasing the potential for exposure to aquatic resources. Aromatics are often further distinguished by the number of rings, which may range from one to six. Aromatics with two or more rings are referred to as polycyclic aromatic hydrocarbons.

*Something that is **Toxic** will induce an adverse effect in a living organism. **Toxicity** is the inherent potential or capacity of a material (in this case crude oil or refined oil products) to cause adverse effects in a living organism (Rand & Petrocelli, 1985).*

Alkenes $C_nH_{(2n-2)}$
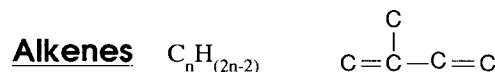
Also called olefins or isoparaffins, alkenes are characterized by branched or unbranched chains of carbons atoms, similar to alkanes except for the presence of double-bonded carbon atoms. Alkenes are not generally found in crude oils, but are common in refined products, such as gasoline.

Oils are further categorized into three broad groups, according to their molecular weight. General statements can be made for each of the three

categories below; however, the reader should be aware that there are always exceptions to generalizations. Crude oils are composed of various combinations of these three categories (light-, medium-, and heavy-weight components) with the following general characteristics:

- **Light-weight components** (low molecular weight)

  - 1 to 10 carbon atoms (C1 to C10);

  - small molecules, with fewer numbers of atoms in each molecule;

  - high VOLATILITY; evaporate and dissolve readily and leave little or no residue because they are simpler in molecular structure (short residence time);

  - many of these components (e.g., benzene) are thought to be more BIOAVAILABLE to animals (primary exposure route: respiratory system);

  - potentially flammable and readily inhaled, and therefore are of concern for human health and safety.

- **Medium-weight components** (medium molecular weight)

  - 11 to 22 carbon atoms (C11 to C22);

  - more complex molecules;

  - evaporate or dissolve more slowly, over several days, with some residue remaining (longer residence time);

  - some medium-weight components are regarded as more toxic than the light-weight components (Clark, pers. comm.; Laferriere, pers. comm.); and

  - not as bioavailable as lower-weight components, so less likely to affect aquatic animals (primary exposure route: respiratory system and readily absorbed through skin).

- **Heavy-weight components** (high molecular weight)

  - 23 or more carbon atoms ($\geq$ C23);

  - undergo little to no evaporation or dissolution (longest residence time);

  - can cause chronic (long-term) effect via smothering or coating as residue in the water column and sediments (tarballs, etc.); primary exposure route: direct topical contact;

  - some heavy-weight components contain carcinogens that absorb through the skin; and

  - risk of exposure is increased due to long residence time, likelihood of contact, and adsorpiton property ("stickiness") of the oil components (Laferriere, pers. comm.).

Examples of Light-Weight Components
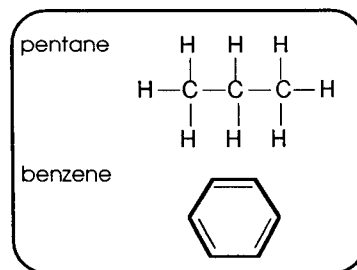
Volatility is a property of a liquid (in this case, an oil or refined product) that has a low boiling point and high vapor pressure at ordinary pressures and temperatures (Morris, 1992). Gasoline is a volatile product that will readily evaporate when spilled in the environment; gasoline has a high volatility.

To be *Bioavailable* is to be in a form that is conducive to uptake by organisms. *Bioavailability* is the tendency of a substance (in this case, oil or individual oil components) to be taken up by a biological organism (Rand and Petrocelli, 1985).

Examples of Medium-Weight Components
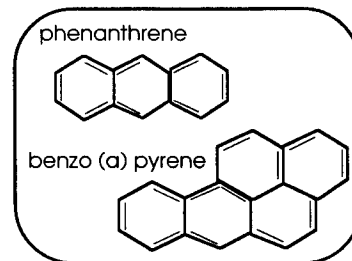
Example of Heavy-Weight Components

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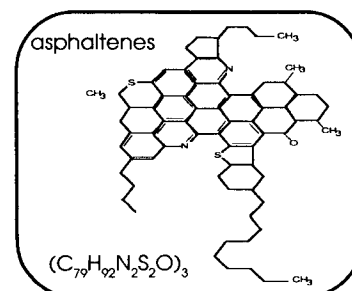
Depending upon their composition, refined petroleum products can be composed of one or more of the three component categories. Figure 1 shows the distribution of various refined products as processed from a "generic" crude oil by carbon number and boiling point range. The quantity of each refined product produced will also vary by oil type. Figure 2 provides an estimated percentage of potential refined products that can be obtained from "generic" light, medium, and heavy crude oils. As the percentage of residual content increases from light to heavy crude oils, the gasoline content decreases because the heavier oils typically contain reduced quantities of the light-weight components. Understanding the type of oil involved in an incident will help you predict an oil's behavior in the environment.
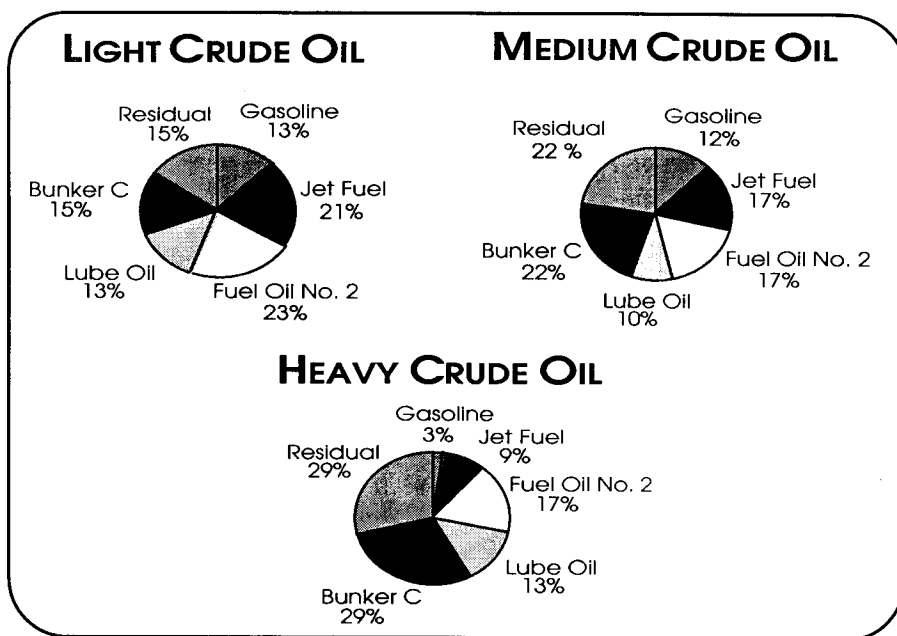
Figure 2. Percentage of refined products resulting from the distillation of three "generic" crude oils. Adapted from Markarian *et al.*, (1993).

OIL CLASSIFICATION

Various systems have been developed to provide additional standardized characterization for oils. In the 33 US Code of Federal Regulations (CFR), Subpart 155.1020, oils are classified into five categories primarily based on their specific gravity. The characteristics for these five groups are based on the relative persistence of oil. Table 3 identifies Group I oils as "NON-PERSISTENT." Groups II through V are all classified as "PERSISTENT" oils. Because Group I oils have a low specific gravity, the regulations do not provide a specific gravity range, they simply list it as not applicable or N/A.

Non-persistent Oils are those refined oil products that will be completely removed from the affected environments through natural weathering processes. They are largely composed of light-weight components. Only short-term impacts are expected from these refined products.

Table 3.   Oil classification categories as defined by 33 US CFR, Section 155.1020.

Category	Persistence	Specific Gravity	Typical Examples
Group I	Non-persistent*	N/A	Gasoline products, condensates
Group II	Persistent **	< 0.85	Diesel-like products and light crude oils
Group III	Persistent	0.85 ≤ 0.95	Medium-grade crudes & intermediate products
Group IV	Persistent	0.95 ≤ 1.00	Heavy crude oils and residual products
Group V	Persistent	> 1.00	Low API gravity products [heavier than pure (fresh) water]

* Non-persistent: a petroleum-based oil that, at the time of shipment, consists of hydrocarbon fractions
-At least 50% or which by volume, distills at a temperature of 340°C (645 °F); and
-At least 95% of which by volume, distills at a temperature of 370°C (700°F).

** Persistent: a petroleum-based oil that does not meet the distillation criteria for a non-persistent oil.

Persistent Oils are those crude and refined oil products that may not be completely removed from an affected environment as a result of weathering processes or clean-up operations; some residue may remain. Persistent oils are composed of a mixture of light-, medium-, and heavy-weight components. Over time, the physical composition of the oil changes as components of the oil are removed through natural weathering processes.

A second, but equivalent way to measure specific gravity was developed by the American Petroleum Institute (API). Called the API gravity scale, it also measures the oil's specific gravity relative to pure water (fresh water), but with this scale, larger values are assigned to lighter products. Table 1 lists the API Gravity Scale for crudes and refined products (Gilfillan, 1993). As can be seen when comparing the information in Table 1 with the data in Figure 1, the greater the amount of light-weight components crude oil or refined products have, the higher its API gravity. Oils and refined products with large amounts of heavy-weight components have lower API gravities.

In an effort to further classify oils, Markarian et al., (1993) compiled a numerical scale for relative persistence of oil and refined products in the aquatic environment (Table 1). This persistence scale was developed by

applying a persistence rating to the oil types listed. In order to provide meaning to the persistence ratings, each persistence value was divided by the least persistent oil product (gasoline) to obtain a scale that ranged from a value of 1 (gasoline; least persistent) to 1600 (residual asphaltenes; highly persistent compounds). As is evident in this table, crude oils and oil products with higher API gravities (refer to Table 1), and consequently higher quantities of light-weight components, are considered relatively non-persistent (Figure 1). Increasing the proportion of medium- and heavy-weight components decreases the API gravity and increases the persistence of the crude oil or refined products.

Purpose of Section III

- *Discuss weathering processes:*
  - *spreading and advection*
  - *evaporation*
  - *dissolution*
  - *natural dispersion*
  - *emulsification*
  - *photo-oxidation*
  - *sedimentation & shore line stranding*
- *For each process, provide answers to the following questions:*
  - *what is it?*
  - *how significant a process is it?*
  - *when does it occur following a spill?*
  - *what properties & ambient conditions influence it?*

What Does This Mean in Terms of Response Operations?

Throughout the spill response, as the oil weathers, response options or methods used must be modified to deal with the changes in the oil. For instance, a disc skimmer that works well on fresh oil will not work as effectively on oil that has emulsified.

SECTION III: FATE AND TRANSPORT PROCESSES WITHOUT CHEMICAL DISPERSANTS

INTRODUCTION

Oil type, weather, wind and wave conditions, as well as air and sea temperature all play important roles in the ultimate fate of spilled oil in the marine environment. After oil is discharged into the environment, a wide variety of physical, chemical, and biological processes begin to transform the discharged oil (Lewis and Aurand, 1997). These chemical and physical changes are collectively called "weathering" and act to change the composition, behavior, routes of exposure, and toxicity of the discharged oil.

There are ten weathering processes discussed in this booklet:

- Spreading and Advection
- Evaporation
- Dissolution
- Natural Dispersion
- Emulsification
- Photo-oxidation
- Sedimentation and Shoreline Stranding
- Biodegradation

Detailed information for each weathering process is provided in the following sections in the approximate order that they dominate the weathering process (both in importance and chronology). Keep in mind that the order in which the processes are presented assumes an instantaneous,

one-time release of oil offshore in a temperate environment. Several of these weathering processes would come into play earlier in the spill chronology if the discharge occurred near the shoreline. In addition, the relative significance of some of these processes would change if the spill occurred under the water surface (as was the case during the *Ixtoc I* blowout), or in tropical or ice conditions.

Weathering processes occur simultaneously; one process does not stop before another begins. This idea is best illustrated in Figure 3 (adapted from Exxon, 1985), which provides a **generic** timeline for weathering. Obviously, some spill-specific conditions determine the duration and significance of certain processes.

In the next sections, answers to the following questions are provided for each weathering process:

- What is it?

- How significant a process is it?

- When does it occur following a spill?

- What oil properties and ambient environmental conditions influence it?
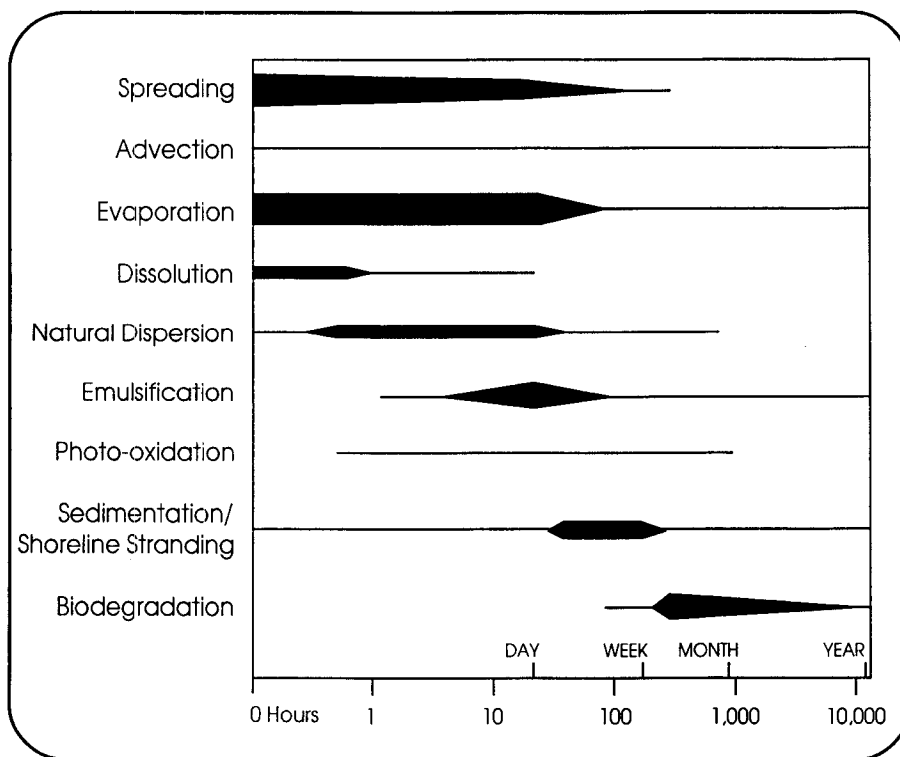
Figure 3.   Relative importance of the weathering processes on a "generic" oil slick over time. The width of the line indicates the magnitude of the process relative to other processes. Adapted from Exxon (1985).

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Summary:
Spreading & Advection

Theoretically, oil released in a single event onto the water surface attempts to spread to become a single slick with uniform thickness. However, during an actual spill event, ambient forces (wind, waves, and currents) act on the slick, often creating a collection of small slicks of various thicknesses or "patches" that spread out over an increasingly larger area.

A **Current** *is defined as a horizontal movement of water; water masses in motion are ultimately driven by energy derived from wind or thermohaline (vertical mixing of different water bodies) circulation (Thurman, 1987).*

Sheen *is a reference to the coloration of oil discharged on water. The color of the slick is based on the thickness of the slick and the refractive properties of light on oil in water (ITOPF, 1981). An oil sheen is typically considered to be less than 0.1 mm in thickness.*

Think of it This Way...

An instantaneous release of 10,000 gallons of Arabian Crude occurs on the open water. The spreading and advection processes work to transfer the oil from a thick, relatively confined slick into a very large, very thin sheen (with an average slick thickness of 0.0152 mm), eventually covering more than 100 square miles of water*.

0.0152 mm sheen = ~100 gal/mile² **

$$\frac{10{,}000 \text{ gal spilled}}{100 \text{ gal/mile}^2} = 100 \text{ miles}^2$$

*This estimate assumes that no other weathering forces are acting on the spilled oil.
**From Gilfillan (1993)

SPREADING AND ADVECTION
WHAT IS IT?

Spreading is the movement of the entire oil slick horizontally on the surface of the water due to effects of gravity, inertia, friction, viscosity, and surface tension (Figure 4). On calm water, spreading occurs in a circular pattern outward from the center of the release point (CONCAWE, 1983). Advection is the movement of the oil due to the influence of overlying winds and/or underlying CURRENTs (NRC, 1985). Spreading and advection increase the surface area of the oil, thereby increasing its exposure to air, sunlight and underlying water (Mielke, 1990). Spreading and advection also increase the potential for impacts, but these weathering processes do not alter the chemical composition of the oil.

Spreading and advection are not uniform, and large variations in oil thicknesses occur within the slick (ITOPF, 1987). Regardless of the oil type, oils tend to spread to a mean thickness of 0.1 mm, with areas of SHEEN and thicker oil patches (Mackay and McAuliffe, 1988); as oil encounters obstructions (shorelines, booms), it will tend to accumulate to form a thicker layer.
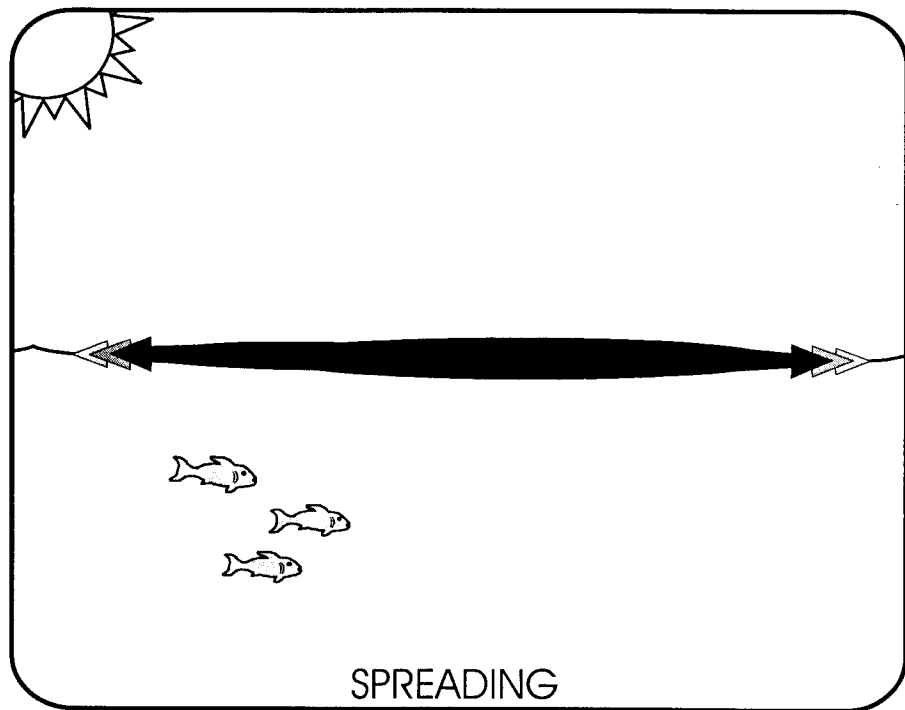
SPREADING

Figure 4. The spreading and advection processes for oil spilled on the water.

How significant a process is it?

Spreading dominates the initial stages of a spill (ITOPF, 1987; Exxon, 1985; CONCAWE, 1983). It involves the WHOLE OIL; this process does not partition the various components of the oil or affect its chemical composition. Spreading makes other weathering processes more efficient because it increases the surface area of a spill.

When does it occur following a spill?

Spreading and advection occur immediately following the release (Mielke, 1990) (Figure 3). They continue for approximately one week to ten days for large slicks, or until the oil is contained by shorelines, collection efforts, or other obstructions (Exxon, 1985). Oil remaining offshore typically forms tarballs and patties after extensive weathering, often floating at or just beneath the surface of the water.

What oil properties and ambient environmental conditions influence it?

- **Specific gravity** – Heavier oils, that is those with high specific gravity and low API gravity, do not spread as readily as a lighter oil (Lewis and Aurand, 1997; ITOPF, 1987; Mielke, 1990).

- **Oil viscosity** – A thicker, less fluid oil will spread less readily (Lewis and Aurand, 1997; ITOPF, 1987; Mielke, 1990; Gilfillan, 1993).

- **Wind speed, sea state, and currents** – These ambient conditions work in concert to transport the oil on the water surface. In general, the slick will move at 3.5 percent of the wind speed (Lewis and Aurand, 1997). As SEA STATE is a function of the wind speed, the greater the wind speed, the greater the sea state; increasing sea state acts to break up the surface slick. Currents play a significant role in the movement of the oil on the water's surface; in conjunction with wind, they work to break up the surface slick into a series of thin parallel patches of oil, called "WINDROWS."

- **Oil pour point** – This is typically a factor only when the product spilled has a high pour point value. If the water temperature is below the oil's pour point, spreading is slowed or prevented (See discussion at right).

- **Seawater temperature** – The temperature of the water can have an impact on the spilled product's viscosity and pour point. This is of minor importance except where it influences pour point (e.g., the water temperature is at or near that of the discharged oil).

Whole Oil is a reference to the oil itself, as a complex product. The reference to "whole oil," is not referring to the individual components of the oil. However, the reader should understand that the "whole oil" will continue to change in composition over time as weathering processes act on it.

Spreading and advection processes do not directly affect the individual components of the "whole oil," they act on the entire product simultaneously, increasing the oil's exposure to additional weathering processes.

Sea state is a description of the ocean surface that compares average wind speed to the resultant height of waves observed in a wave train, using a numerial code ranging from 0 (1 to 3 knot winds) to 5 (20 to 24 knot winds) (Thurman, 1987; Kucklick and Aurand, 1995).

Windrows are rows of floating debris (oil) aligned parallel to the direction of the wind that result from natural circulation patterns (Thurman, 1987).

How Pour Point Affected the *Presidente Rivera* Spill

In 1989, the motor vessel Presidente Rivera spilled an oil product into the Delaware River. The pour point of the product was greater than the temperature of the water, so the spilled oil "congealed into (wax-like) globules in which 90 percent of the oil was not visible from the surface" (Overstreet and Galt, 1995).

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Salinity is the salt content of the water. Salinity of typical seawater ranges from 32 to 35 parts per thousand.

- **Salinity** – SALINITY is a minor factor in spreading and advection. As salinity influences the density of the seawater (increasing salinity, increases density), it will affect the buoyancy of the oil. If an oil's density is near that of the surrounding water, it can assume a neutrally buoyant position (neither sinking nor floating on top) within the water column, thereby reducing the oil's ability to spread.

EVAPORATION

Summary: Evaporation

Evaporation is the primary weathering force in the removal of the oil from the sea surface (dependent upon oil type). As much as 50 to 60 percent of the spill volume can be lost to the atmosphere within the first few days of the spill. However, this process physically and chemically changes the structure of the remaining oil components, often making these remaining components more difficult to deal with during response operations. Evaporation is enhanced by the spreading process; as more of the oil is exposed to the air-oil interface, evaporation rates continue. Warm air and water temperatures, high-level wind velocities, and solar heating all increase the evaporative process.

WHAT IS IT?

Evaporation is the preferential transfer of light- and medium-weight components of the oil from the liquid phase to the vapor phase (into the atmosphere) (Exxon, 1985). In other words, oil components with low boiling points will readily evaporate from the slick's surface (Mielke, 1990; ITOPF, 1987) (Figure 5). Most people who have pumped their own gas at a service station have accidentally discharged small quantities of gasoline onto their cars or the ground, only to have the spilled gasoline disappear in a matter of moments. Gasoline is composed exclusively of light-weight components that are highly volatile and rapidly evaporate.
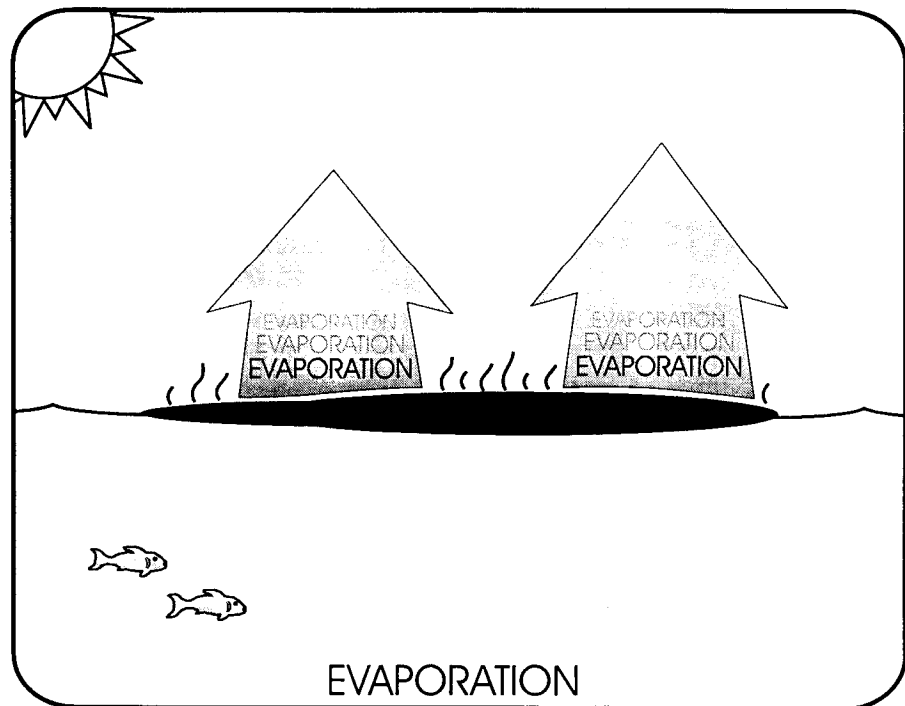

Figure 5. The evaporation process for oil spilled on the water.

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The chemical composition of the slick is physically altered as these components evaporate from the spilled oil. Although the volume of the oil decreases through evaporation, the remaining components of the oil have a greater viscosity and specific gravity (Lewis and Aurand, 1997), which leads to a thickening of the oil and contributes to the formation of tar balls, tar mats, etc.

HOW SIGNIFICANT A PROCESS IS IT?

Evaporation is the primary weathering process involved in the natural removal of oil from the sea surface (Figure 3). During the first 24 - 48 hours, it is the single most important weathering process from the standpoint of volume reduction of the spill (Payne and McNabb, 1984).

Depending on the oil composition, evaporation may be responsible for the loss of more than half of a surface slick's volume over time. A 20 to 40 percent loss by volume of product to evaporation is considered normal for crude oils following a release (Mielke, 1990; Lewis and Aurand, 1997). The percentage lost to the environment through evaporation can be even greater for light crude oils and refined products because of the higher amount of light-weight components contained in them. Evaporation can account for a 75 to 100 percent loss in volume for many light-weight refined products (e.g., gasoline and kerosene) (Lee, 1980; ITOPF, 1987).

Evaporation also affects an oil's toxicity; many of the light-weight components within oil (C1 to C8) are generally considered the most toxic because they are considered more bioavailable. These components often undergo evaporation within the first five hours (Lewis and Aurand, 1997). Recently, Exxon Biomedical Sciences, Inc. (EBSI) found evidence that the greatest toxicity lies in the C10 to C12 fraction of the oil (Clark, pers. comm.). Although these medium-weight components also undergo evaporation, they do so at a somewhat slower rate compared with the C1 to C8 components. Thus, the C10 to C12 fractions of the oil remain in the water longer and have the potential of resulting in injury.

WHEN DOES IT OCCUR FOLLOWING A SPILL?

Evaporation starts immediately following the discharge and continues for a period of approximately two weeks. For all oils, the majority of the total evaporation occurs within the first 12 hours (McAuliffe, 1989). The lighter components undergo evaporation at a faster rate; within 48 to 72 hours, floating oil will have lost nearly all the light-weight components (C15 and under) with boiling points of less than 270°C (Jordan and Payne, 1980; Lee, 1980). Spills of refined products (kerosene and gasoline) may evaporate completely within a few hours, while light

Think of it This Way...

A 10,000 gallon spill of Arabian Crude occurs instantaneously on the open water. During the first week of the spill, the spreading and advection processes have spread the slick out over 100 square miles (refer to Spreading and Advection for more information). If during the first few days, the oil undergoes a 50 percent volume reduction from evaporation, there would be only 5,000 gallons of oil remaining on the water and it would cover an area of 50 square miles with a sheen thickness of 0.0152 mm.* Instead of a 10,000 gallon spill, only 5,000 gallons of the oil remains on the water.

* assumes no other weathering processes are acting on the spilled oil.

crudes can lose up to 40 percent within the first 24 hours (ITOPF, 1987). Heavier components (with more complex molecules) may remain in surface slicks for several weeks prior to the chemical changes that allow them to evaporate; for these oils the evaporative process may continue for as long as a year for oil that remains in the environment. However, after the first week, the rate of evaporation is greatly reduced (Figure 3).

WHAT OIL PROPERTIES AND AMBIENT ENVIRONMENTAL CONDITIONS INFLUENCE IT?

- **Oil composition and oil volatility** – The greater the proportion of components with low boiling points, the greater the evaporation of those components.

- **Surface area of slick** – Spreading enhances the evaporative process. The greater the amount of oil exposed to the air, the higher the rate of evaporation. Thinner, bigger slicks will evaporate better than thick, smaller slicks of the same oil type and volume.

- **Solar radiation** – The sun's energy causes an increase in the oil's surface temperature (heating), increasing the evaporative process as more components vaporize. Evaporation continues under cloudy conditions and at night, but at a reduced rate.

- **Wind speed, sea state** – Wind blowing over the slick's surface will increase evaporation. Increasing wind speed and increased sea state can cause some of the oil to form a spray or mist, which also evaporates quickly.

- **Water temperature** – Like solar radiation, evaporation increases with increasing water temperature. If ambient water temperatures remain above the oil's pour point, the oil will remain fluid, allowing the spreading process, and ultimately the evaporation process, to continue.

DISSOLUTION

WHAT IS IT?

Dissolution is the transfer of oil components (not the "whole" oil) from a slick on the surface into solution in the water column (Exxon, 1985). Certain light-weight components of the spilled oil tend to be the most soluble, and, therefore, the ones that dissolve in the water column. (Figure 6).

HOW SIGNIFICANT A PROCESS IS IT?

Dissolution is relatively insignificant in the overall weathering process in terms of reducing the volume of the spill. Only a slight fraction of the oil dissolves; it has been estimated that only 2% to 5% of a spill is removed by natural dissolution (Neff, 1990). For some oil types, dissolution of even a few percent is unlikely (NRC, 1985). This is because many of the same components that could dissolve would typically evaporate first. Evaporation and dissolution are in direct competition for the same oil components, but with evaporation occurring 10 to 1,000 times faster than dissolution (CONCAWE, 1983; ITOPF, 1987; Lewis and Aurand, 1997). Even when components do dissolve into the water column, they may be removed by subsequent evaporation (Mackay and McAuliffe, 1988) or other weathering processes such as biodegradation or photo-oxidation (refer to these sections for more information).

Summary: Dissolution

Dissolution is in direct competition with evaporation, and therefore plays a relatively minor role in the overall weathering process of oil on the water. In general, less than five percent of the oil dissolves into the water column and the majority that does dissolve eventually undergoes evaporation from the water into the atmosphere. The oil components that do dissolve are usually considered toxic and become bioavailable to species in the water column. However, the area of exposure is typically localized and limited in duration due to the natural mixing and dilution within the water column.

Think of it This Way...
An instantaneous release of 10,000 gallons of Arabian Crude occurs in the open water. Dissolution of the surface slick typically accounts for 2 to 5 percent of the oil removal from the water's surface (Neff, 1990). Potentially, 200 to 500 gallons of oil could be removed through this weathering process.
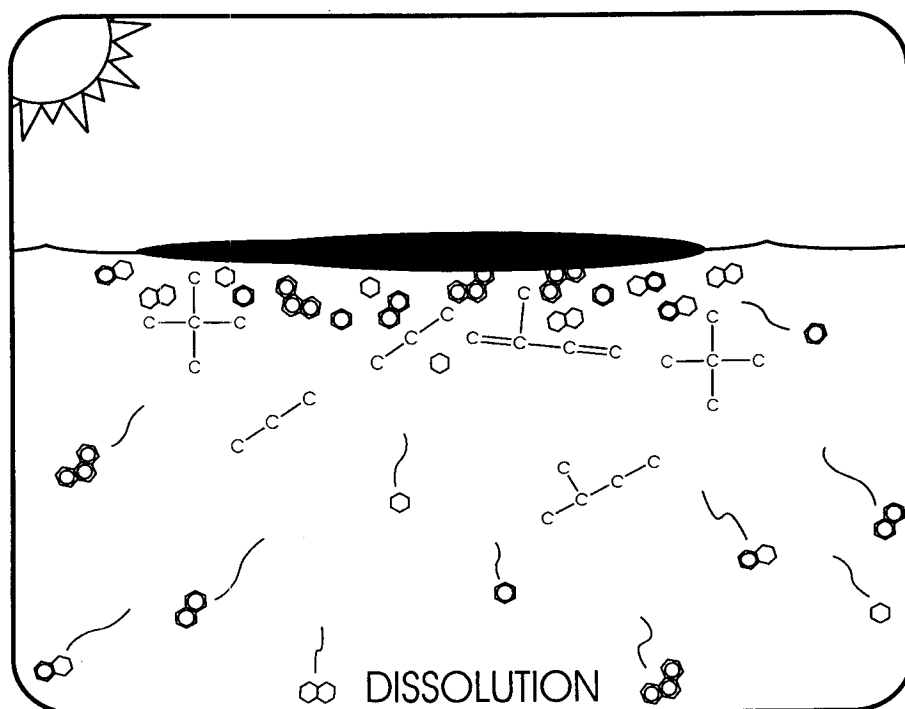
Figure 6. The dissolution process for oil spilled on the water.

The portions of the oil that dissolve into the water column (primarily those components that are in a ring-like structure and many of the light-weight components) are typically the more acutely toxic components (NRC, 1985). Although only a very small amount of the spilled oil dissolves, once dissolved, these components are in a bioavailable form (Neff, 1990) and if exposed to marine life, can cause environmental impacts/injuries. The largest concentrations of the dissolved toxic components are found near the surface, close to the oil spill release point; therefore the threat of toxic exposure to marine life in the water column is considered localized and short-lived due to evaporation and mixing in the water column (NRC, 1989).

WHEN DOES IT OCCUR FOLLOWING A SPILL?

Dissolution typically occurs only within the first 24 hours of a spill (Figure 3).

WHAT OIL PROPERTIES AND AMBIENT ENVIRONMENTAL CONDITIONS INFLUENCE IT?

- **Water solubility** – Most of the dissolved hydrocarbons are the more soluble light-weight components that are classified as aromatic hydrocarbons (C1 to C10). The dissolution process preferentially depletes light-weight components with low-boiling point hydrocarbons in a "ring" form (aromatics hydrocarbons) because of their greater solubilities. An oil with greater concentrations of these aromatic hydrocarbons would more likely lose a higher percentage of its volume to dissolution.

- **Water temperature** – Components that dissolve in cold water or under ice conditions can remain in solution for a longer period of time because evaporation is reduced (Lee, 1980).

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NATURAL DISPERSION

WHAT IS IT?

Natural dispersion is the process of forming small oil droplets that become incorporated into the water column in the form of a dilute oil-in-water suspension (Exxon, 1985; CONCAWE, 1983). This process occurs when breaking waves mix the oil into the water column. Large droplets (greater than 0.1 mm in diameter) that are formed when mixing occurs tend to "coalesce, rise rapidly, and concentrate near the water surface. Small droplets (typically less than 0.1 mm in diameter) break away from the main mass and become dispersed in the water column" (Neff, 1990).

Dispersion reduces the volume of the slick at the surface but does not change the physicochemical properties of the oil (CONCAWE, 1983). The "whole" oil is mixed into the water column in these small droplets (Figure 7).

HOW SIGNIFICANT A PROCESS IS IT?

Following evaporation, natural dispersion is the most important process in the breakup and disappearance of a slick (Neff, 1990). Based on observations from actual spills, the percent of oil lost from the remaining slick due to natural dispersion has been estimated to range from 10 to 60 percent per day for the first three days of the spill, depending on

Summary: Natural Dispersion

Natural dispersion is one of the most important weathering processes during the first days of the spill. Dispersion is dependent on natural mixing or turbulence forces generated by wind and waves. Droplets of the "whole" oil, not just components of the oil, get mixed into the water column. Depending on the droplet size, the oil may resurface, join with other droplets and resurface, or mix (permanently) into the water column. Natural dispersion prevents further reductions in the spill volume for several of the weathering processes but may enhance others. Naturally dispersed oil may be well mixed within the water column, and this essentially makes the "whole" oil bioavailable to subsurface species.

Think of it This Way...

An instantaneous release of 10,000 gallons of Arabian Crude occurs on the open water. Conservatively, a 10 percent per day loss due to natural dispersion over the first three days of the spill could be expected under moderate seas (Sea State of 2-3). This translates into a 2,710 gallon loss to natural dispersion over a three day period.*

Day 1: 10,000 gal x 0.10 = 1000 gal
Day 2: 9,000 gal x 0.10 = 900 gal
Day 3: 8,100 gal x 0.10 = 810 gal

* assumes no other weathering processes are acting on the spilled oil.

Figure 7.   The natural dispersion process for oil spilled on the water.

the sea state (the higher the sea state, the higher percentage dispersed) but independent of oil type (CONCAWE, 1983).

WHEN DOES IT OCCUR FOLLOWING A SPILL?

Dispersion begins soon after the oil is spilled onto the water surface. This weathering process reaches a maximum rate in approximately 10 hours following a spill but may continue for several weeks (Exxon, 1985; Neff, 1990) (Figure 3). Within 100 hours following a spill, dispersion overtakes spreading as the primary mechanism of transport of oil from the spill site (Neff, 1990).

WHAT OIL PROPERTIES AND AMBIENT ENVIRONMENTAL CONDITIONS INFLUENCE IT?

Cohesion is the attraction between the molecules of a liquid that enables drops and thin films to be formed (Morris, 1992).

Interfacial Tension is the surface tension at the interface of two liquids (Morris, 1992). Think of it as water on a newly waxed car (wax is petroleum-based). When water hits a waxed car, the water will bead up. If the car is still dirty or has a soap film on it, then the water won't bead up. The higher the interfacial tension, the more the water will bead.

Surface Tension is the stretching force required to form a liquid film (Morris, 1992).

Surfactants are often referred to as surface active agents. Surfactant molecules contain both water-compatible (hydrophilic) and oil-compatible (lipophilic or hydrophobic) portions that orient themselves at the oil-water interface so that the oil-compatible portion of the molecule attaches to the oil and the water-compatible portion of the molecule faces outward into the surrounding water. This surfactant mechanism diminishes the interfacial tension between the oil and the water and enhances the breakup of the oil into droplets (when combined with wave action) as well as stabilizing the resultant oil droplets.

- **Oil viscosity** – Very liquid oils and refined products [oils with a viscosity of less than 2,000 centistokes (cSt)] undergo dispersion easily. More viscous oils disperse less readily. In general, any oil with a viscosity greater than 20,000 cSt (e.g., residual fuel oils that must be heated during transporation and pumping) will not be dispersed naturally. As oil evaporates or weathers, viscosity increases and natural dispersion decreases.

- **Sea state** – Energy is required to mix the oil into the water column. Strong winds which cause breaking waves are the primary forces generating natural dispersion. Wind speeds greater than 10 knots are required for the natural dispersion of oil droplets into the water column (NRC, 1989). In general, the rougher the sea, the greater the chance for natural dispersion to occur.

- **Slick thickness** - COHESION of the oil increases with the thickness of the slick. The thicker the slick, the harder it is for natural dispersion processes to break the oil into small enough droplets so that the oil can remain suspended in the water column. Natural dispersion occurs more often with thinner slicks because the amount of turbulence (wind and wave action) required to disperse the oil is less.

- **Oil/water interfacial tension** - INTERFACIAL TENSION affects the oil's ability to break up into smaller droplets and its ability to recoalesce. With a lower interfacial tension, the oil is more likely to form oil droplets and less likely to recoalesce.

- **Presence of naturally occurring surfactants** - Many oils have naturally occurring SURFACTANTS which aid in the dispersion of the oil into the water column. These surfactants will naturally align themselves in the oil to facilitate droplet formation and to prevent recoalescence (Neff, 1990).

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EMULSIFICATION

WHAT IS IT?

Emulsification is the mixing of seawater droplets into oil spilled on the water's surface (water-in-oil emulsion) (Figure 8). As a surface slick undergoes evaporation, some of the heavier components tend to precipitate out of the oil mixture in the form of very fine, solid particles. These particles assist in stabilizing a water-in-oil emulsion because of the pres-

Summary: Emulsification

Emulsification is the incorporation of water into the oil, forming a new product which is relatively resistant to other weathering processes (such as evaporation and dissolution). Since water is being added to the oil, emulsification also tends to increase the total volume of oil remaining in the environment, often by a factor of two to three. In short, emulsification prevents the other weathering processes from reducing the oil and can cause the spill volume to increase.
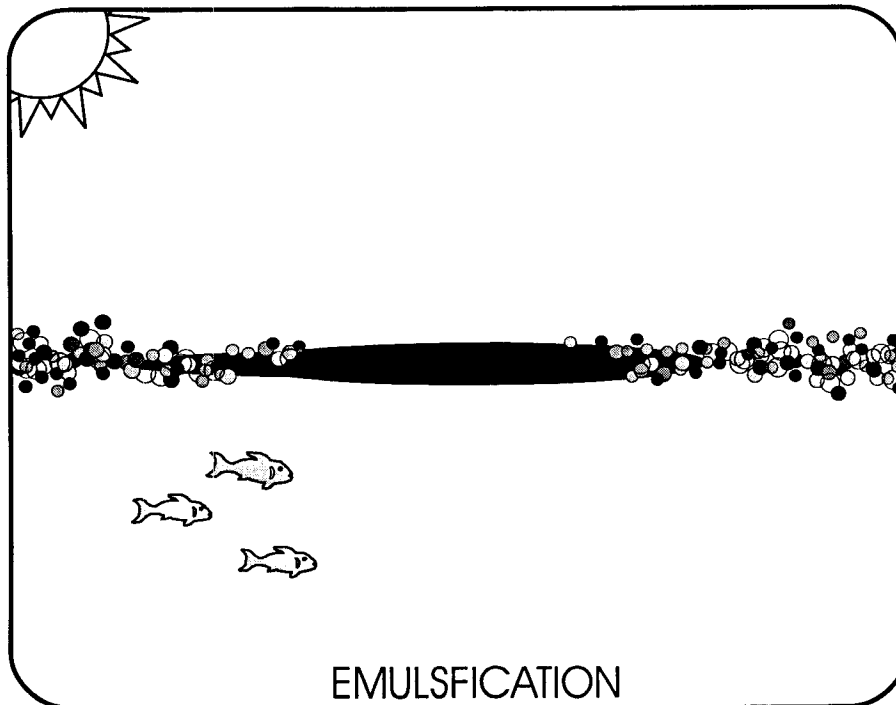
EMULSFICATION

Figure 8. The emulsification process for oil spilled on the water.

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ence of natural surfactants (Lewis and Aurand, 1997). Emulsions typically contain 30 to 80 percent water and are often referred to as "mousse" due to their color and consistency (Neff, 1990; Mielke, 1990; Gilfillan, 1993). Water-in-oil emulsions are highly viscous and have densities approaching seawater (Mackay and McAuliffe, 1988).

HOW SIGNIFICANT A PROCESS IS IT?

Once a mousse has formed, the weathering of the oil can be significantly reduced; the majority of the weathering processes are slowed when a stable emulsion is formed (ITOPF, 1987; Neff, 1990). In the open ocean, 10-20 percent of the heaviest components within an oil typically form tarballs, lumps, patties or tar mats, depending on the oil type and environmental conditions present following the release. The development of a stable emulsion would preclude the formation of the typical endpoints for spilled oil (tarballs, lumps, patties, and tar mats).

Emulsification can greatly increase the total volume of oil while inhibiting all other natural weathering processes (which act to reduce the spill volume) and the effectiveness of most response options. Emulsified oils:

- often have a volume more than three times greater than the same volume of oil alone (CONCAWE, 1983);
- may become more viscous and sticky (Lewis and Aurand, 1997);
- resist being separated back into oil and water; and
- result in difficult clean-up and disposal issues for decision-makers for very stable emulsions.

Over time, the mousse remaining on the water or stranded on the shoreline can result in the formation of tar lumps or patties; hard, weathered exteriors with gooey, slightly liquid centers (think of a Cadbury® chocolate egg).

WHEN DOES IT OCCUR FOLLOWING A SPILL?

Emulsification often begins during the first day of the spill and can continue to occur throughout the first year (Figure 3). The largest volume of mousse is typically formed within the first week of the spill, after loss of the lighter-weight components to evaporation and dissolution has occurred (Lee, 1980).

WHAT OIL PROPERTIES AND AMBIENT ENVIRONMENTAL CONDITIONS INFLUENCE IT?

- **Oil composition and viscosity** – Typically more viscous, heavy-weight oils, that have very large asphaltene and wax contents, tend to form stable water-in-oil emulsions. These very

stable emulsions "do not break down under the influence of stand-ing, shearing, heating, or treatment with chemicals... [while other, less viscous oils] produce weak emulsions which easily revert to the oil residue and water" (Lewis and Aurand, 1997). Emulsion formation is also more likely with oils containing natural sur-factants. Emulsions almost never form during spills of gasoline, kerosene, and diesel fuels (except under very cold conditions) (NRC, 1989; RPI, 1992).

- **Sea state** – Natural mixing energy is required to suspend the water into the oil for the formation of emulsions. The greater the mixing energy, the faster an emulsion will be formed, and the greater the volume of water that can be incorporated into the emulsions. Emulsions are less likely to be formed under calm sea conditions (CONCAWE, 1983).

PHOTO-OXIDATION

WHAT IS IT?

Photo-oxidation is when sunlight (ultraviolet and near-ultraviolet areas of the spectrum), in the presence of oxygen, transforms hydrocarbons through photo-oxygenation (increasing the oxygen content of a hydro-carbon component) into new by-products (Mielke, 1990) (Figure 9).
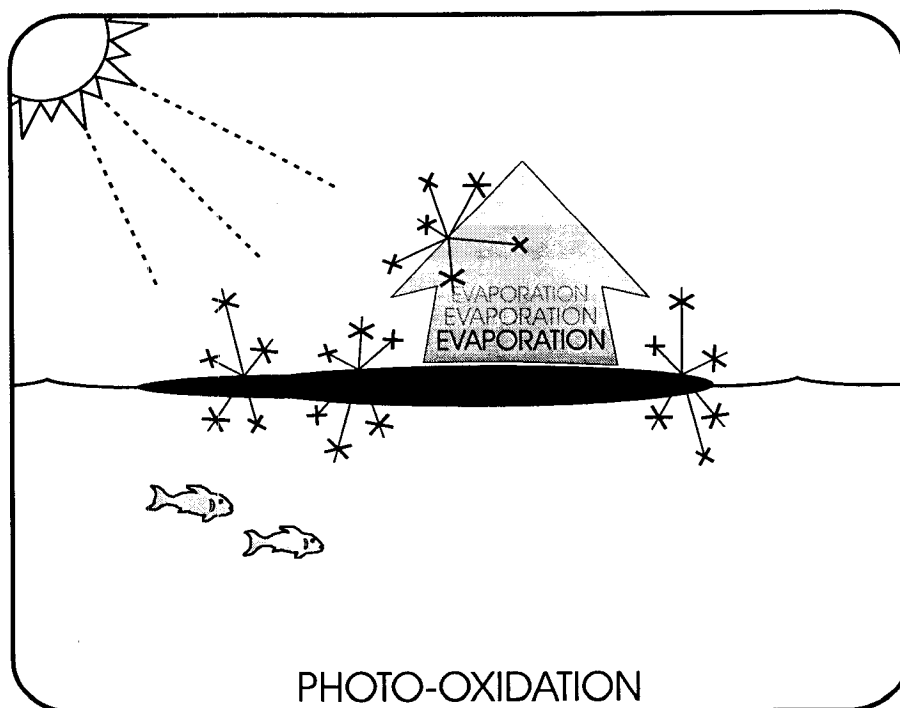
PHOTO-OXIDATION

Figure 9. The photo-oxidation process for oil spilled on the water.

Summary: Photo-oxidation

Photo-oxidation is the process by which components in oil are chemically transformed through a photo-chemical re-action (in the presence of oxy-gen) to produce new com-pounds which tend to be more water-soluble and toxic (in the short-term) than the parent compounds (Neff, 1990). Un-der strong solar conditions (low latitude, few clouds) this weathering process has been shown to decompose a thin slick in a matter of a few days (NRC, 1985). With increasing latitude or water depth, the sunlight intensity decreases, re-sulting in a reduction in the amount of oil that can be photo-oxidized. As this is a so-lar energy driven process, photo-oxidation is inhibited by cloud cover and stops alto-gether at night.

Photo-oxidation occurs only at the very surface of the oil and directly on components which have physically separated from the whole oil. The ultimate fate of these by-products is removal to and dissipation into the atmosphere and water column. Many of these by-products are water soluble and can readily enter the water column. Fortunately, these by-products typically have half-lives of just a few hours to a few days, as they are degraded by further photolytic action and are subject to dilution into the water column (Payne and McNabb, 1984).

Furthermore, some of the newly formed by-products are more toxic than the parent compounds (Mielke, 1990; Neff, 1990); as a result, localized impacts to natural resources as well as response personnel may become an issue. Photo-oxidation also produces heavy-weight by-products that are not soluble in oil or water (Neff, 1990).

Photo-oxidation of the surface slick results in changes in the interfacial properties of the oil, affecting spreading and mousse formation, and may result in the transfer of the toxic by-products into the water column due to the by-product's enhanced water solubility (Mackay and McAuliffe, 1988). As the soluble products are typically diluted in the water column through natural mixing, the concentrations of the photo-oxidative trans-formed by-products will be relatively low (Mackay and McAuliffe, 1988).

How significant a process is it?

The photo-oxidation process plays a relatively minor role in the overall weathering of the spilled oil (ITOPF, 1987) as it is interrupted by nights and lessened on cloudy days (Mackay and McAuliffe, 1988). Some studies have shown that under strong sunlight, thin films of oil on the water break down at rates of no more than 0.1 percent per day (ITOPF, 1987). Other work, however, has found that this weathering process can decompose a thin slick in a matter of a few days (NRC, 1985).

When does it occur following a spill?

Photo-oxidation can begin within several hours following a spill and last for several weeks to a month (Figure 3). Photo-oxidation differs from other weathering processes in that it doesn't peak at any one time. It is typically limited by light intensity, duration, weather conditions, and the extent of emulsification.

What oil properties and ambient environmental conditions influence it?

- **Intensity of sunlight** – Photo-oxidation is limited at high latitudes where there is less sunlight, especially during winter. Strong, summer sun increases the rate of photo-oxidation. Photo-

oxidation of the surface slick is inhibited by cloud cover and precipitation. Many large spill events are the result of bad weather, so the photo-oxidation process would be considerably reduced initially.

- **Physical state of the oil on the water surface** – Rough sea states have the tendency to mix the oil into the water column. As light intensity decreases with water depth, the rate of photo-oxidation will also decrease as more of the oil is mixed into the water column. Oil that has undergone extensive evaporation or that has become emulsified may have a reduced ability to undergo photo-oxidation.

- **Surface area of oil exposed to sunlight** – The greater the surface area of the oil exposed to sunlight, the more likely the oil will undergo photo-oxidation. This is true for both oil on the water surface as well as for that portion of dispersed and dissolved oils that are affected by sunlight in the water column.

SEDIMENTATION AND SHORELINE STRANDING

WHAT IS IT?

Oil, especially the heavier components, is sticky. It tends to adhere (become glued to) particles in the water column,on shorelines, and on the seafloor bottom. Sedimentation is the incorporation of oil within both suspended and bottom sediments (Figure 10). Sedimentation usually occurs with the heavy-weight components of the oil which do not dissolve in the water. In general, oil adheres to detrital particles (particles which are mixtures of organic matter, bacteria, and small clay particles). Sedimentation also occurs when marine organisms ingest naturally dispersed oil droplets in the water column. The oil droplets pass through the organism undigested and are eliminated as part of the fecal matter. Sedimentation can also occur when oil is stranded on shore and then becomes incorporated with sediments and subsequently transported to subtidal environments. Very heavy or weathered oil can sink directly to the bottom without sorption onto sediments first; this process is enhanced as the density of the water is lowered by the influx of fresh water (ITOPF, 1987; Neff, 1990).

Shoreline stranding is the visible accumulation of petroleum along the water's edge(shoreline) following a spill. This "beached" oil can contribute to the volume of oil undergoing sedimentation as the stranded oil becomes sediment laden, sinks, or becomes buried along the shoreline.

**Summary:
Sedimentation and
Shoreline Stranding**

Sedimentation of oil can occur essentially three ways: sorption onto sediments; deposition as fecal pellets after consumption by marine organisms; or by direct sinking as a result of increased density of the oil after extensive weathering. Once on the bottom, the oil often becomes buried. This burial process effectively stops all weathering processes. Sedimentation can begin almost immediately following the release; however, it is often a function of the spill's location; suspended sediments and presence of marine organisms are typically more prevalent in the nearshore environment.

Shoreline stranding is the accumulation of petroleum along the water's edge following a spill. Currents, winds and waves, and tidal cycles are important factors in the transportation of the oil onto the shore. Permanent stranding and burial can occur as tidal cycles, weather events, and sediment transport actions change and progress.

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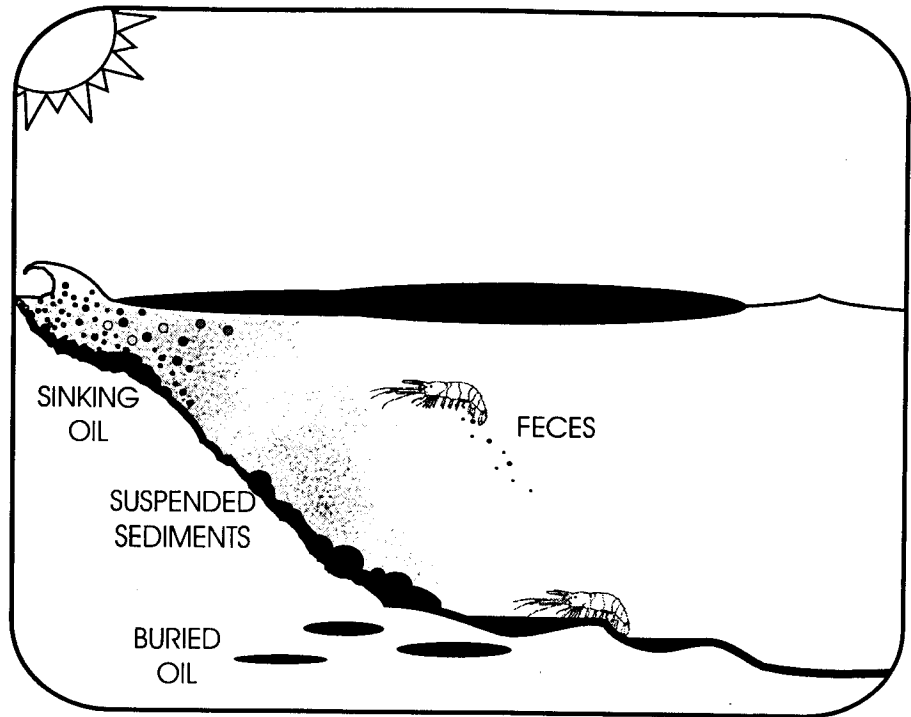
Figure 10. The sedimentation process for oil spilled on the water.

How significant a process is it?

Sedimentation is a very important process in shallow, rough sea conditions where bottom sediments are repeatedly resuspended (Exxon, 1985). "The greater the suspended sediment load, the more oil may be adsorbed and transported to the bottom. Approximately 120-300 mg of petroleum may adsorb to each kilogram of suspended clay" (Neff, 1990). Sedimentation effectively removes oil from additional weathering processes, including natural biodegradation (to be discussed in the next section). As has been found during several spills, the most persistent oil residues were those that were incorporated into subtidal sediments of estuaries or nearshore waters (Gundlach *et al.*, 1983), or those stranded on low energy shores (Hayes *et al.*, 1993). During the *Exxon Valdez* oil spill, the oil that penetrated the cobble-boulder beach sediments, remained essentially unweathered five years later (Michel and Hayes, 1996). Shoreline stranding is affected by the proximity of the spill to the affected shoreline, intensity of current and wave action on the affected shoreline, and the persistence of the spilled product.

WHEN DOES IT OCCUR FOLLOWING A SPILL?

Sedimentation can begin almost immediately following a spill but increases and peaks several weeks into the spill (Figure 3). Shoreline stranding is typically a function of the distance from the spill to the shore, the prevailing wind and currents, and the chemical nature of the spilled oil.

WHAT OIL PROPERTIES AND AMBIENT ENVIRONMENTAL CONDITIONS INFLUENCE BOTH SEDIMENTATION AND SHORELINE STRANDING?

*   **Amount of suspended sediment in the water column**
    – Water depth and physical energy affect the amount of suspended sediment in the water column. Shallow water depths are likely to have high concentrations of both suspended particles and microscopic organisms which can accelerate the sedimentation rate of oil particles as they sorb onto these particles. In offshore, DEEP WATER environments, the suspended sediment load in the top 10 meters of the water column is greatly reduced relative to the nearshore environments. Therefore, sedimentation due to the sorption of the oil onto these particles is unlikely. One exception for deep water environments is where several water bodies meet (e.g., the Gulf Stream or Mississippi River delta); this mixing zone often has high quantities of sediments and other floating debris that could increase the sedimentation potential.

A high-energy, nearshore environment typically will have the necessary combination of suspended particles (sediments and microscopic organisms) and wave action that lead to sedimentation. Low-energy areas are not likely to undergo sedimentation until after the oil has undergone extensive weathering; however, in intertidal areas, the oil can be stranded on the shoreline and become buried by depositional beach cycles. Extensively weathered oil sinking as a result of increasing density relative to the surrounding waters is a very rare occurrence. Another event that has the potential to significantly affect sedimentation rates is when oil is released near the ocean floor (e.g., through a hole on the bottom of a grounded or sunken vessel); oil rising to the surface can pick up suspended sediments.

Wind, wave and current patterns affect shoreline stranding of the oil. Onshore winds act to push surface slicks on shore. Wave action combined with tidal cycles can strand the oil on beaches until the next tidal cycle, when the oil is often lifted off intertidal sediments. Currents are also responsible for the transportation

For More Information.....

Internationally, there have been at least ten significant spill incidents reported where oil initially floated and then sank (Michel and Galt, 1995). Two of the most recent cases were the Bouchard 155 (1993) and the Morris J. Berman (1994). In the Bouchard 155 incident, 325,000 gallons of No. 6 fuel oil (API gravity 10-11) was released at the entrance to Tampa Bay, FL. The oil initially floated and a significant amount was recovered. However, following a small storm where the oil was mixed into the water column and picked up suspended sediments, thick mats of submerged oil were found in the nearshore subtidal habitats (Michel et al., 1995).

In 1994, the barge, Morris J. Berman, grounded within a few hundred meters of shore off of San Juan, Puerto Rico and released 750,000 gallons of a Group V oil (API gravity 9.5). Within 24 hours of the spill, submerged oil was reported. Initially the oil floated; however, because the oil was spilled in the surf zone, an estimated 20 percent of the oil quickly mixed with sand, became negatively buoyant and sank. This oil tended to refloat every afternoon when the winds picked up (Michel et al., 1995; Michel and Galt, 1995).

***Deep Water** is defined as a marine habitat with a water column depth greater than 10 meters (Kucklick et al., 1997).*

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of oil to shore. However, at the same time, high energy by waves and currents can also work to keep the oil offshore.

- **Quantity of oil stranded on the shoreline** – In spills where large quantities of oil come ashore all at once, there is a greater chance of sedimentation. Permanent stranding and burial can also occur as the tidal cycles change (from high-high tides to low-high tides). Storm events can also work to strand/bury oil on the shoreline, often well above the high-high tide line.

- **Specific gravity** – The higher the specific gravity, the less sediment is needed for the oil to sink. Many of the very heavy oils (Group V oils) will not float in fresh water.

Summary: Biodegradation

This weathering process occurs when naturally occurring bacteria and fungi consume petroleum hydrocarbons as a food source, essentially transforming existing molecules into oxidized by-products that will eventually be further degraded through oxidation to carbon dioxide and water. This is a slow process which begins to occur after detoxification of the spilled oil via other weathering processes and after the resident microbe population has grown and multiplied, often taking several weeks to get established. For the most part biodegradation is limited by nutrient and oxygen availability, and microbes work best in moderate temperatures.

BIODEGRADATION

WHAT IS IT?

Biodegradation is the process where naturally occurring bacteria and fungi consume hydrocarbons to use as a food source. Carbon dioxide and water are excreted as waste products. This weathering process occurs on the water surface, in the water column, in sediments, and on shore (Atlas, 1981). Microbes (bacteria and fungi) which can utilize hydrocarbons, are found naturally in the marine habitats; however, they grow and multiply after an oil spill occurs because additional food sources (carbon) become available following a spill (Figure 11).

HOW SIGNIFICANT A PROCESS IS IT?

Biodegradation is a significant process; however, it is also a slow one. For stranded oil, biodegradation becomes a dominant factor once the toxic components of the oil have been removed by physical processes below a threshold value (Fucey and Oudot, 1984). Neff (1990) reports that biodegradation rates have been estimated to be 1 to 10 mg/m^3/day in the open ocean, and 50 mg/m^3/day in the upper 5 cm of intertidal sediments along the Brittany coast of France; at the 50 mg/m^3/day biodegradation rate, scientists have estimated that it would be nearly 20 years before the 64,000 tons of oil that washed up along the French coastline would be removed through the biodegradation process (Neff, 1990). It is the dominant weathering process for the light- and medium-weight components remaining after the other weathering processes have stopped or have been greatly reduced. Because many of the heavy-weight components of the spilled oil are so complex structurally, they
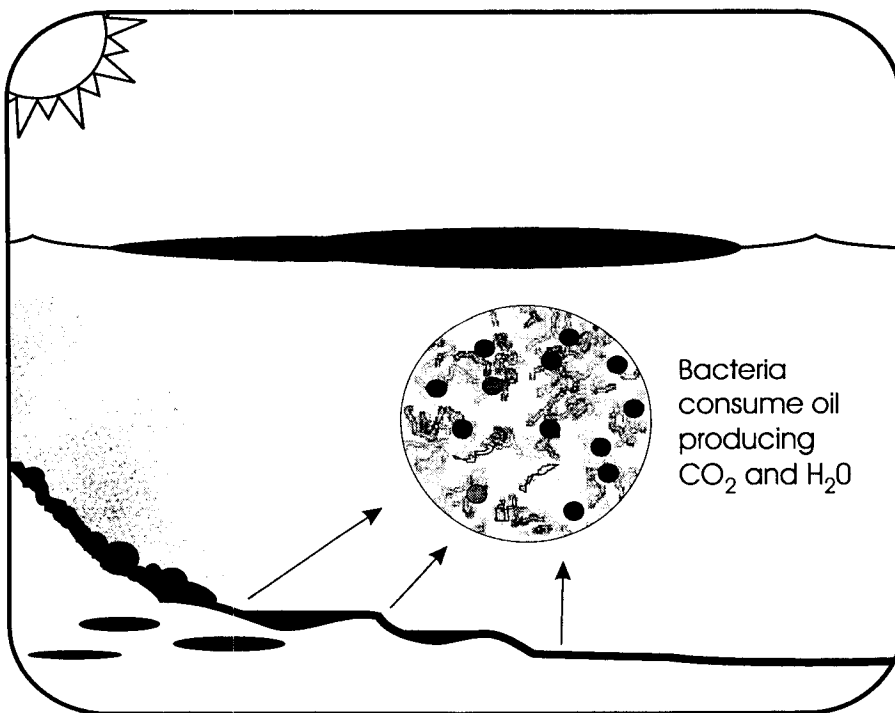
Figure 11. The biodegradation process for oil spilled on the water. During consumption, the ultimate waste products generated are carbon dioxide and water.

are often not susceptible to biodegradation until after periods of months or years have passed; many of these compounds are considered biologically inert (RPI, 1992).

WHEN DOES IT OCCUR FOLLOWING A SPILL?

The biodegradation process can begin quickly following a spill and will continue as long as degradable hydrocarbons persist (Figure 3). Some research suggests that there is a lag time between when the spill occurs and when the microbes begin to degrade the oil. This is most likely due to the fact that the oil is initially toxic to the microbes; after weathering of the toxic components, the microbes can begin consuming the oil's hydrocarbons (Hoff, 1992).

The microbial degradation typically peaks within the first month following a spill. Following a release, the microbial populations in the spill area undergo rapid growth. Eventually, the microbes can become limited by the amount of nutrients (such as nitrogen and phosphorus) and oxygen present in the environment (Hoff, 1992). With the addition of nutrients to affected shorelines, a microbial population can continue to increase in number resulting in a faster rate of oil degradation.

WHAT OIL PROPERTIES AND AMBIENT ENVIRONMENTAL CONDITIONS INFLUENCE IT?

- **Abundance and variety of existing hydrocarbon-degrading microorganisms** – Areas with chronic oil pollution problems (spills, auto runoff, etc.) will have higher oil-degrading microbe populations than areas that are considered more pristine (free of human pollution) (ITOPF, 1987).

- **Water temperature** – The biodegradation process is slowed in cold waters. It takes approximately four times longer to degrade the same volume of oil at 4°C (40 °F) as it does at 18°C (65 °F) (Leblanc, 1990). As in many aquatic animals, cold water slows the metabolism of the microbes. Furthermore, in very hot, shallow water environments, microbial degradation of oil in sediments can be reduced due to heat stresses (Lewis and Aurand, 1997).

- **Nutrients** – Microbes require nutrients, including water, nitrogen and phosphorus for continued growth. If nutrients are limited, then the microbial population is limited in its ability to grow and multiply.

Aerobic refers to the presence of oxygen.

- **Oxygen** – The majority of microbes live in an AEROBIC environment. They require oxygen to biodegrade petroleum hydrocarbons; these microbes feed in areas where oxygen is normally plentiful (e.g., water column, water surface, sediment surface, etc.). There are also microbes that degrade petroleum hydrocarbons in areas that lack oxygen (e.g., subsurface sediments), but at a very low rate. Oil in ANAEROBIC environments may degrade very little, with oil persisting often for several years (Hoff, 1992).

Anaerobic refers to the absence of molecular oxygen.

- **Oil composition** – Certain oils are better suited as microbe "food." They contain petroleum hydrocarbons that are readily degraded by the microbes. Oils and refined products which contain large quantities of heavy-weight components may not undergo biodegradation as the molecules are too large and complex for the microbes to degrade.

- **Water salinity** – Salinity has little effect on the microbes' ability to degrade oil. However, areas with extremely high salinities have been shown to inhibit biodegradation. Under the normal ranges of salinities likely to be encountered in US marine waters, the problem of high salinities inhibiting microbial degradation is considered unlikely (Lee and Levy, 1989).

Interaction of the Fate and Transport Processes

In the real world, these weathering processes do not occur separately, but simultaneously as they overlap each other through the course of an oil spill. The processes interact and affect each other, and in turn affect the properties of the spilled oil (CONCAWE, 1983) (Figures 3, 12, and 13). The following are examples of some of the common interactions between the processes. This list is by no means complete but serves as a general guide to the major interactions.

- Evaporation, dissolution, dispersion, emulsification, photo-oxidation, and biodegradation are enhanced by spreading.

- Much of the oil that evaporates is then photo-oxidized in the atmosphere.

- As evaporation occurs, the tendency of the slick to emulsify is enhanced, forming thick sludge and tar balls.

- Most of the oil components that do dissolve into the water column will eventually leave the water and enter the atmosphere through the evaporation process, or they are biodegraded.

- Natural dispersion reduces the volume of a slick on the surface, thus reducing evaporation.

- Natural dispersion exposes subsurface marine organisms to the "whole" oil; this oil may undergo sedimentation as a result of being consumed and reprocessed as fecal matter.

- Naturally dispersed oil is biodegraded.

- Naturally dispersed oil droplets can bind to suspended sediments, causing the new oil/sediment complex to undergo sedimentation.

- As the slick becomes emulsified and thickens, surface area is reduced, consequently evaporation is reduced.

- Emulsification inhibits spreading, evaporation, and natural dispersion and slows photo-oxidation and biodegradation.

- Oil that is stranded on shore tends to persist there or be eroded.

Summary:
Interaction of Processes

The weathering processes discussed in the previous section do not occur as separate events. Instead, they occur either simultaneously or overlap each other. Additionally, some of the processes will alter or affect the rate of others. For instance, as evaporation occurs, emulsification is enhanced.
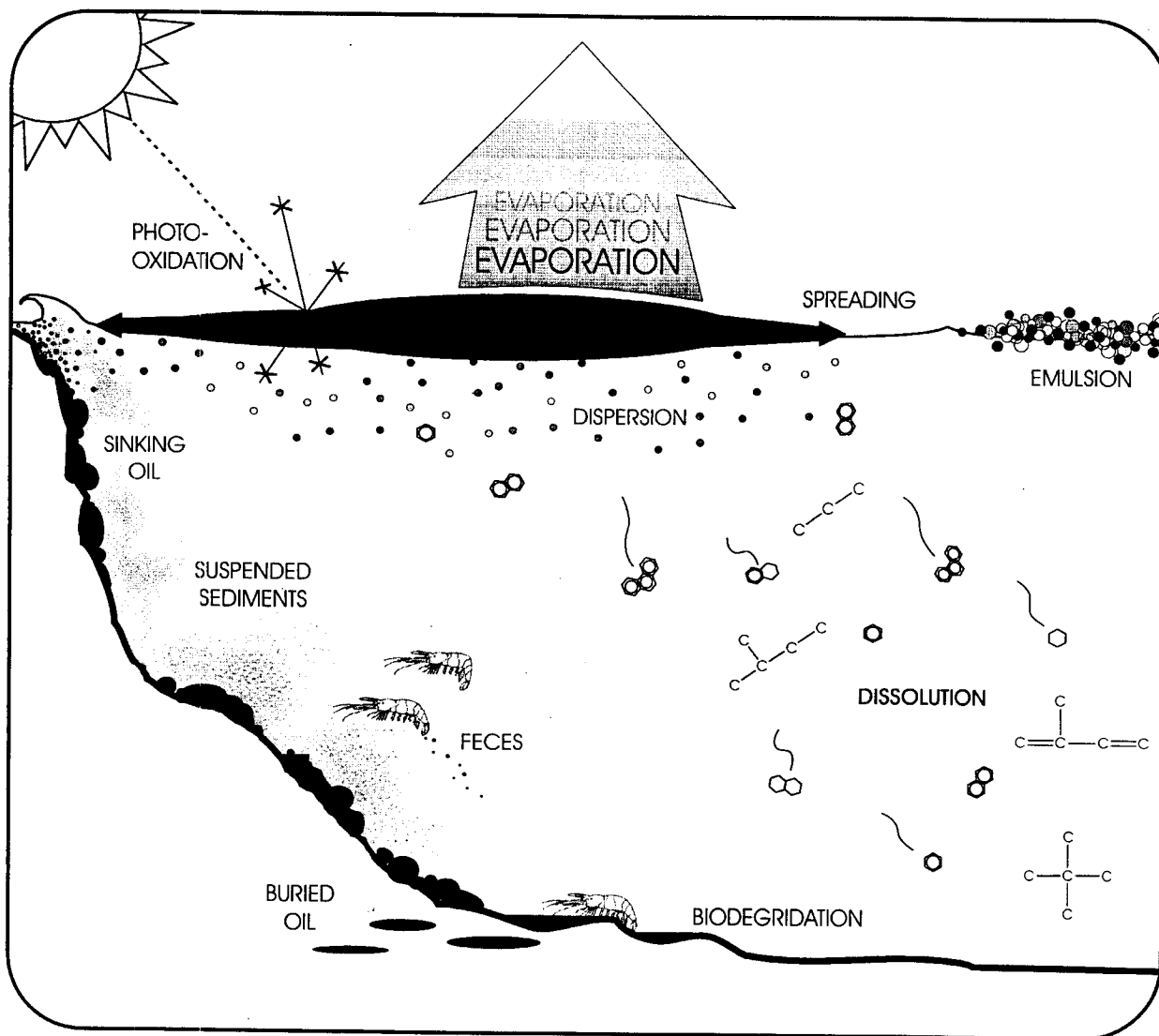
Figure 12. Summary figure outlining the ten weathering processes for oil spilled in the marine environment. Shoreline Stranding is not depicted.
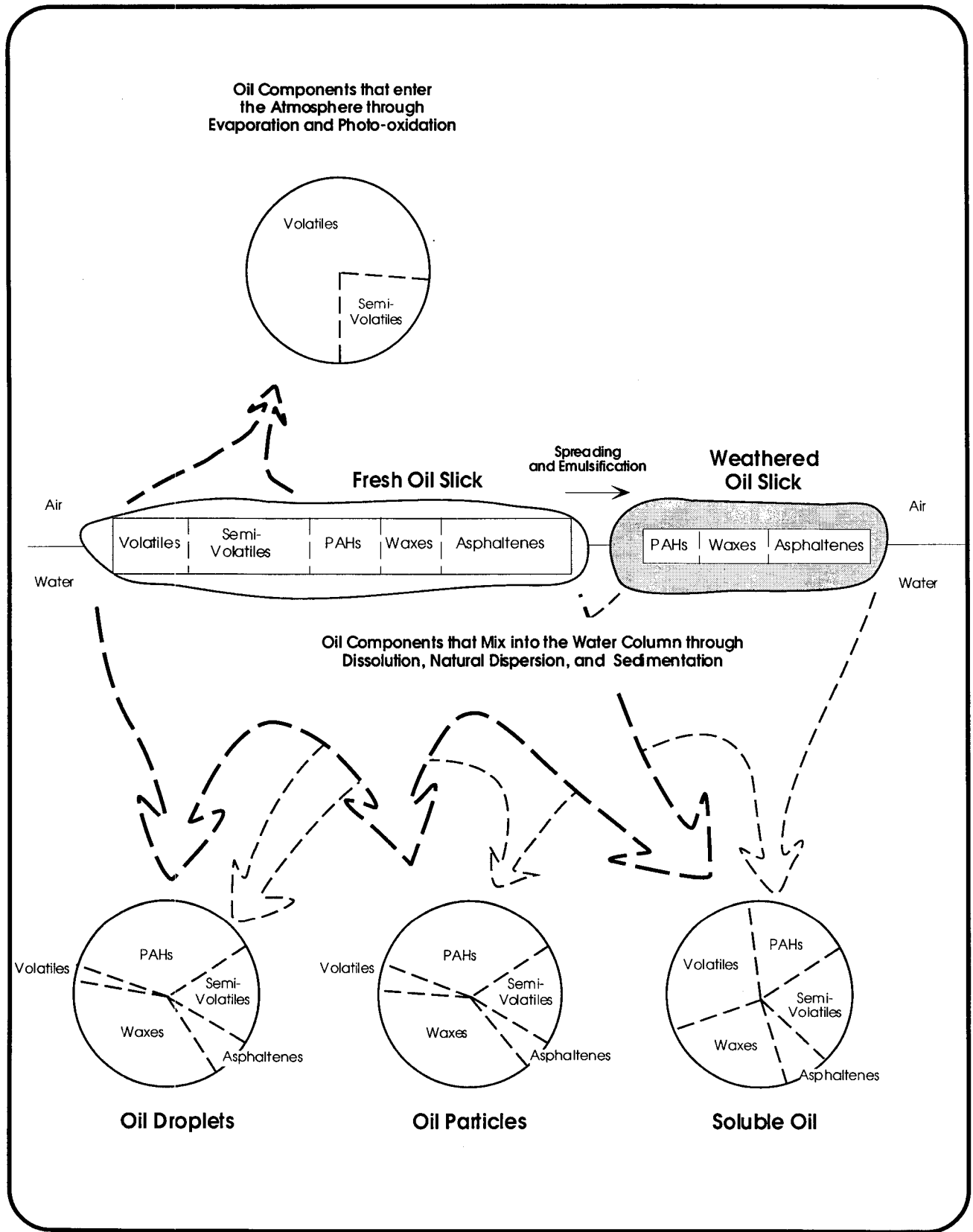
Figure 13. Summary figure outlining the partitioning of oil components oil spilled in the marine environment. [Adapted from Lewis and Aurand (1997).]

Purpose of Section IV
• Briefly define dispersants.
• Discuss how dispersants affect or alter the various fate processes.

Section IV: Fate and Transport Processes With the Use of Chemical Dispersants

What are Dispersants?

Dispersants are chemicals composed of surface active agents (surfactants), solvents, and stabilizing agents (i.e., agents which act at the oil/water surface). Dispersants work because the surfactants in dispersants contain water-compatible and oil-compatible components which allow them to concentrate at the boundary between the oil and water (Figure 14). These surfactants reduce the interfacial tension of the water and promote the break-up of the slick into fine droplets, facilitating the dispersion of the oil into the water column. Surfactants also act to prevent the recoalescence of suspended, chemically dispersed oil droplets. Another advantage of the use of chemical dispersants is that these products affect an oil's viscosity; they reduce the amount of energy necessary to disperse the oil into the water column (NRC, 1989; ITOPF, 1987; Gilfillan, 1993; Neff, 1990).

Dispersants work best when they are applied to oil that has not weathered, or not weathered much. Therefore, there may be a narrow window of opportunity for an effective application of chemical dispersants shortly after the oil is spilled. Although it varies by oil type, dispersant applications are generally considered to be effective for oil that has been on the water less than 72 hours (Pond et al., 1997b).

Additional, more detailed information regarding dispersant technology is provided in the second booklet in this series, "A Decision-maker's Guide to Dispersants: A Review of the Theory and Operational Requirements." It provides answers to frequently asked questions, including: How do these chemicals work? Why should they be used? Under what conditions would chemical dispersants be appropriate for use? and What are the operational issues involved with chemical dispersant applications?

The following provides a summary of the general impact(s) that chemical dispersants can have to the individual fate and transport processes that affect oil spilled on the water. The extent of impacts will vary depending on the oil type and environmental conditions.
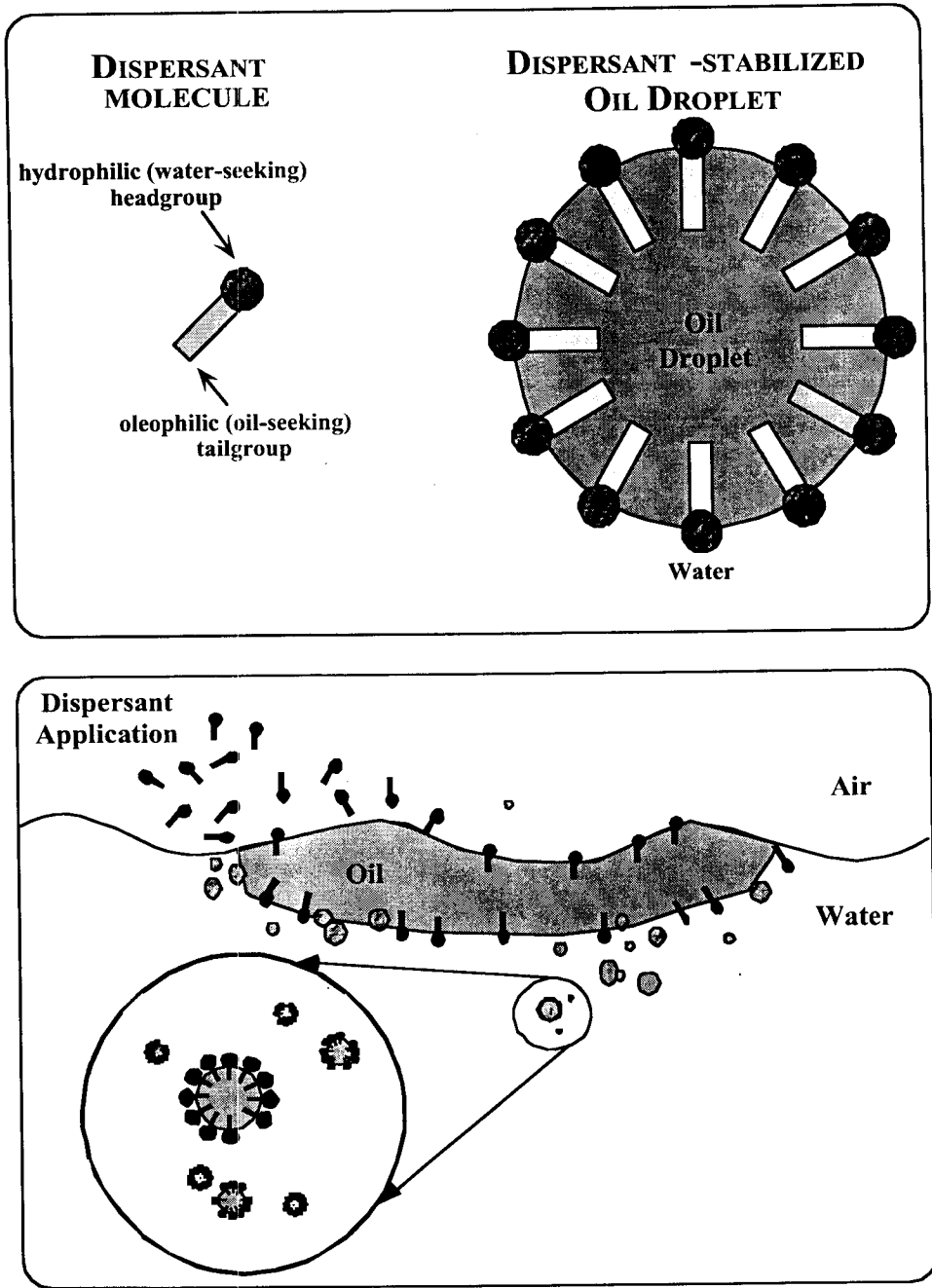
Figure 14. The mechanism of chemical dispersion.

THE EFFECT OF CHEMICAL DISPERSION ON SPREADING AND ADVECTION

Spreading is enhanced with the application of dispersants.

Spreading is initially enhanced with the application of dispersants, although for the first few seconds after application, spreading is retarded because the surfactant lowers the surface tension of the water, thereby causing the oil slick to contract, resulting in an initial herding effect (NRC, 1989).

THE EFFECT OF CHEMICAL DISPERSION ON EVAPORATION

To date there are conflicting results on the effect that chemical dispersants have on the evaporation process. One study found that chemically dispersed oil appeared to weather in a manner similar to oil naturally dispersed, while another study found that there was enhanced evaporation with chemically dispersed oil (NRC, 1989). In general, if dispersants are applied properly, evaporation will be reduced because the oil will be removed from the water's surface. With chemically dispersed slicks, evaporation will primarily occur as a secondary weathering process. Dissolved components from the chemically dispersed oil droplets can be removed from the water column to the atmosphere through evaporative forces.

THE EFFECT OF CHEMICAL DISPERSION ON NATURAL DISSOLUTION

The application of chemical dispersants will probably increase the rate of natural dissolution as the oil is broken up and dispersed into the water column. This is because surface slicks that are chemically dispersed expose more of the oil's surface area to the water column; thus the dispersed oil has a greater potential to undergo the dissolution process.

THE EFFECT OF CHEMICAL DISPERSION ON NATURAL DISPERSION

Chemical dispersants supplement the natural surfactants in the oil to enhance natural dispersion. Because the application of chemical dispersants causes a reduction of the interfacial tension between the oil and water, the wave energy or turbulence required for natural dispersion is reduced. Once chemically dispersed into the water column, the oil is more bioavailable; the hydrocarbons and thus their effect on the water column environment are increased.

THE EFFECT OF CHEMICAL DISPERSION ON EMULSIFICATION

Emulsification will normally decrease with the addition of chemical dispersants because water-in-oil emulsions are destabilized or broken up by the surfactants in chemical dispersants (NRC, 1989). Some dispersant formulations may function first as emulsion inhibitors, effectively lengthening the window of opportunity for dispersant use by as much as several days under certain conditions.

THE EFFECT OF CHEMICAL DISPERSION ON PHOTO-OXIDATION

The photo-oxidation process is probably slowed as dispersants act to remove the oil from the surface of the water. As sunlight intensity is the dominant factor for photo-oxidation, removal of the oil from the water's surface would inhibit this process. In turn, because evaporation processes are also reduced with the addition of dispersants, the photo-oxidation of the evaporation by-products would also be affected.

Photo-oxidation is probably reduced with the application of chemical dispersants.

THE EFFECT OF CHEMICAL DISPERSION ON SEDIMENTATION AND SHORELINE STRANDING

For the range of oils on which dispersants are considered effective, the small oil droplets formed by chemical dispersion are considered less sticky than naturally dispersed droplets. Because of this reduction in "stickiness," chemically dispersed droplets are also considered less susceptible to sedimentation (NRC, 1989). Heavy oils and refined products that would be expected to sink in the water are not good candidates for dispersant application; however, if dispersants were applied, it is unlikely that they would have an effect on these oils.

Sedimentation and Stranding is reduced with the application of chemical dispersants.

Chemically-dispersed oils and refined products are less likely to strand when the dispersants have been properly applied, based on field trials comparing untreated and chemically dispersed oils (API, 1986).

THE EFFECT OF CHEMICAL DISPERSION ON BIODEGRADATION

Chemical dispersion enhances biodegradation of the oil. The microbes have greater access to the oil because there are now many more droplets with greater total surface area present.

Biodegradation is enhanced with the application of chemical dispersants.

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SECTION V: IN CONCLUSION

From reading this booklet, you should have obtained a basic understanding of:

- physical and chemical properties of oil.
- the various processes that weather oil.
- the significance of these processes in moving and changing the oil.
- the various conditions that influence each process.
- how dispersants influence weathering.

Why is this information useful to you, as a decision-maker? You will probably never be directly asked about the fate and transport of oil. However, having a general understanding of it will help you in making informed decisions when planning for and responding to oil spills. It should allow you to better visualize the changes in volume, chemical content, and behavior of oil as it moves through the environment. This information is also useful when trying to get a better understanding of dispersants as well as exposure and effects of oil and dispersed oil in the environment.

We encourage you to read the other two booklets in this series, "A Decision-makers Guide to Dispersants: A Review of the Theory and Operational Requirements" and "Defining the Links Between Fate and Transport Processes with Exposure and Environmental Effects of Oil and Chemically Dispersed Oil."

If you want more information on fate and transport processes, you should refer to the bibliography in Section VI. Most of these references go into great detail on specific fate processes, and provide useful diagrams and figures.

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