


A DECISION-MAKER'S GUIDE TO DISPERSANTS

A REVIEW OF THE THEORY AND OPERATIONAL
REQUIREMENTS

HEALTH AND ENVIRONMENTAL SCIENCES DEPARTMENT
PUBLICATION NUMBER 4692
MARCH 1999

 American
Petroleum
Institute

 STEP
Strategic for Total's
Environmental Partnership

A Decision-Maker's Guide to Dispersants

A Review of the Theory and Operational Requirements

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4692

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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, the 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 untreated, 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 dispersant booklets:

1. Fate of Spilled Oil in Marine Waters: Where Does It Go? What Does It Do? and How Do Dispersants Affect It?
2. A Decision-maker's Guide to Dispersants: A Review of the Theory and Operational Requirements.
3. 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 second in the series.

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OVERVIEW

- The American Petroleum Institute (API) commissioned the preparation of three booklets to help bridge the gap in the understanding of dispersant use, effectiveness, and effects.
- This booklet (second in the series) focuses on chemical dispersant technology and the information needs of decision-makers when attempting to make informed decisions regarding the use of chemical dispersants, their potential benefits and risks.
- Crude oil is a complex mixture of thousands of different compounds, composed primarily of carbon, hydrogen, sulfur, nitrogen, and oxygen. Hydrocarbons (composed solely of carbon and hydrogen atoms in various combinations) are the most abundant compounds found in crude oils.
- Dispersants are chemicals composed of surface-active agents (surfactants) and solvents. The surfactants in the dispersants 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. They act to prevent the re-coalescence of suspended, chemically dispersed oil droplets.
- The solvent component of chemical dispersants assists surfactants in the penetration and alignment within the oil.
- Dispersants are designed to break up surface slicks and disperse the oil as fine droplets into the water column immediately under the slick. These chemically dispersed droplets will be further diluted within the water column as the droplets are subjected to natural dispersion through advection forces. Chemical dispersants lower the water interfacial tension, thus enabling wave action to transfer the oil from one location (the water surface) to another (spread out within the water column).
- An energy source (often in the form of wave action) is required to mix the chemically dispersed oil droplets into the water column. Some of the smaller oil droplets can remain dispersed in the water column for a long time.
- Use of dispersants is considered a viable response technique as they may:
 1. reduce the overall impact of oil on many habitats;
 2. prevent oil from stranding on sensitive shorelines and other economically important resources (e.g., boats, marinas, shellfish beds);
 3. reduce potential damage to birds, marine mammals, and other natural resources that could be impacted by oil on the water surface;
 4. provide a clean-up option when other response techniques are less effective (e.g., waves too high for booms and skimmers);
 5. enhance microbial degradation and evaporation by increasing the surface area of the oil droplets;
 6. remove the oil from the action of the wind that may ultimately bring the oil ashore; and
 7. reduce the formation of tarballs and mousse.

- There is a greater potential that resources that exist in the water column (e.g., fish) will be exposed to chemically dispersed oil droplets than if the slick were to remain untreated on the water surface (note that there are exceptions to every generalization). Exposure potential is greatest directly under the slick and would diminish with depth and distance from the oil source.
- Chemically dispersed oil droplets (generally less than 10 to 20 microns in diameter) will remain in the water column for extended periods of time, where the chemically dispersed droplets will undergo natural weathering processes (dissolution, biodegradation).
- Concentrations of oil dispersed under slicks are typically greater when oil is chemically dispersed than if left to naturally disperse. Naturally dispersed oil concentrations are typically measured in the 100–500 ppb (0.1–0.5 ppm) range for the upper three meters of the water column under freshly spilled and/or released oils. Peak concentrations of chemically dispersed oil in the upper three meters of the water column are typically less than 10 ppm, but have been measured for brief periods in the 20–50 ppm range; these concentrations are generally greater than those measured for natural dispersion, by a factor of 40 or more.
- Pre-spill planning is necessary to facilitate the use of chemical dispersants during actual spill response decision-making.
- The decision to use chemical dispersants is based on several factors affecting each incident, including:
 1. environmental issues: sea state, salinity, water temperature, and specific issues related to the ecosystem at risk;
 2. oil issues: chemical composition of the oil, the degree of weathering the oil has undergone; and
 3. dispersant issues: federal and state approval for use, availability, and application personnel and strategy.
- Application rates are important; the average recommended dispersant-to-oil ratio is 1 to 20. However, during recent spills off Great Britain, dispersant-to-oil application ratios averaged from 1 to 65 to as little as 1 to 80. In order to disperse heavy or weathered oils, a dispersant to oil ratio greater than 1 to 20 may be necessary.
- Several application systems have proven to be effective in applying chemical dispersants (vessel-based, fixed wing aircraft or helicopter systems). Applying chemical dispersants effectively requires trained and skilled personnel.
- Following a dispersant application, it is valuable to monitor the application to determine if the dispersant was applied at the appropriate dosage in the correct locations, if the dispersant is working effectively, and if there are any obvious (qualitative) ecological effects. Data obtained from monitoring are used to improve future dispersant use decision-making through long-term data gathering.

INTRODUCTION

Consider this...an oil tanker has grounded offshore, releasing some or all of its cargo. It is your job to recommend response options to protect the sensitive nearshore environment. One of the recommendations that you are considering is the use of chemical dispersants on the already expanding surface slicks. You need a concise, complete, and easy-to-use summary of dispersant technology, to refresh your memory and support your decisions. This booklet is designed to fill that need.

Purpose of Section

- *Introduce the subject.*
- *Discuss the purpose and organization of the booklet.*

PURPOSE OF BOOKLET

This booklet was developed for oil spill response decision-makers, to provide an accurate summary of chemical dispersant technology. To make informed decisions on using dispersants, or any countermeasure, it is important first to have a clear understanding of the potential benefits and risks.

- How do these chemicals work?
- Are they safe to use?
- Why should they be used?
- Under what conditions are chemical dispersants appropriate?
- What are the operational issues involved with chemical dispersant applications?

All of these answers are found in this booklet, in an easy-to-use format supplemented with diagrams and figures. To address chemical dispersant technology fully, this booklet has been divided into three parts.

Part I provides a brief review of oil chemistry: more details can be found in the first booklet in this series, "Fate of Spilled Oil in Marine Waters: Where Does It Go, What Does It Do, and How Do Dispersants Affect It?"

Part II provides a detailed discussion on chemical dispersants and their mechanism of action. This section briefly compares and contrasts chemical dispersion with natural dispersion and dissolution.

Part III comprehensively reviews the operational issues associated with chemical dispersant applications, including: application rates and variables that affect these rates, equipment needs, effectiveness issues, monitoring issues, and application limitations and restrictions.

PART I: OIL CHEMISTRY REVIEW

Purpose of Part I

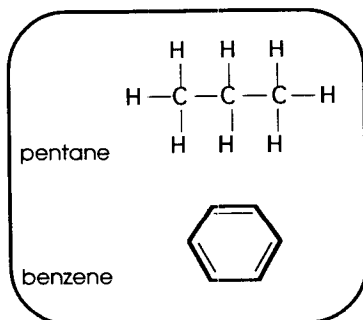
- To review information on general oil properties.

Hydrocarbons are chemical compounds found within crude oils and refined products that are composed solely of carbon and hydrogen atoms in various combinations. Hydrocarbons are the most abundant compounds found in crude oils; up to 85 percent.

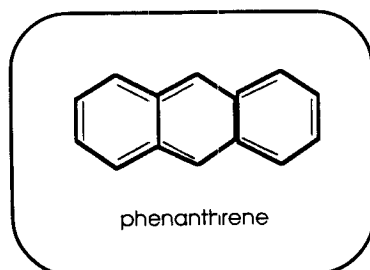
Trace Metals, such as nickel, vanadium, iron, aluminum, sodium, calcium, copper and others, are chemical elements typically found in small quantities in petroleum.

Asphaltenes and Waxes are complex hydrocarbons that contain trace elements in their structure; these compounds are considered relatively inert and resistant to most weathering processes.

Examples of Light-weight Molecules Found in Oil



Example of Medium-weight Molecules Found in Oil



The chemical components and characteristics of crude and refined oils are reviewed in this section. An individual oil's chemistry influences dispersion processes and dispersant effectiveness. Being familiar with oil chemistry will help you interpret the specific data for your response decisions. General properties are reviewed below. A more detailed discussion, especially concerning physical oil properties and oil classification, can be found in the first booklet in this series "Fate of Spilled Oil in Marine Waters: Where Does It Go, What Does It Do, and How Do Dispersants Affect it?"

WHAT IS OIL?

Oil is not one "thing"; it is a complex and highly variable mixture of compounds (Lewis and Aurand, 1997). Crude oil is a complex mixture of mainly HYDROCARBONS, and to a smaller extent compounds containing TRACE METALS. Hydrocarbons (including ASPHALTENES and WAXES) are the most abundant compounds in crude oil (NRC, 1989; Gilfillan, 1993). In general, there are essentially three groups of hydrocarbons in every oil:

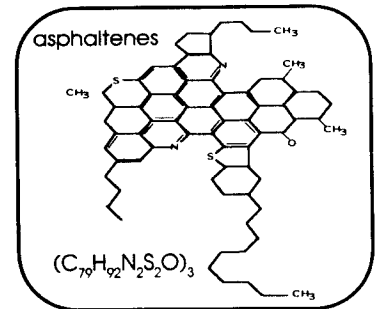
- **Light-weight components** (low molecular weight)
 - 1 to 10 carbon atoms (C1 to C10);
 - small number of atoms in each molecule;
 - evaporate and dissolve rapidly (hours) and leave little or no residue because they are simple in molecular structure;
 - many of these components (e.g., benzene) are thought to be readily absorbed by animals through the skin or through inhalation; and
 - potentially flammable and readily inhaled by people, and so 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;

- sometimes regarded as more toxic than the light-weight components (Clark, pers. comm.); and
- not as bioavailable as lower-weight components, so less likely to affect animals.
- **Heavy-weight components** (high molecular weight)
 - 23 or more carbon atoms ($\geq C_{23}$);
 - undergo little to no evaporation or dissolution; and
 - can cause chronic (long-term) effects via smothering or coating as residue in the water column and sediments (tar balls, etc.) (Helton, 1996).

Crude oils are composed of various combinations of the three hydrocarbon categories. When comparing crude oils, the concentration of the larger molecular compounds (medium- and heavy-weight relative to the amount of light-weight components) within the oil affects PERSISTENCE; oils with greater concentrations of medium- and heavy-weight components will typically result in increased persistence (Table 1). Oils composed primarily of the light-weight components are usually considered NON-PERSISTENT.

Refined products are typically composed of a narrow range of processed components, usually containing the lighter-weight components (e.g., gasoline, condensates, and diesel-like products). RESIDUAL or LOW API GRAVITY OIL PRODUCTS are primarily composed of heavy-weight components sometimes mixed with a blending agent (No. 2 fuel oil is a common blending agent) in the development of these heavy re-

Examples of Heavy-weight Molecules Found in Oil



Persistence refers to an oil or refined product's tendency to remain in the environment following a discharge for a long period of time.

Persistent Oils are those crude and refined oil products that cannot be completely removed from an affected environment as a result of weathering processes; some residue remains. In general, an oil with a weathering half-life of months to years is considered persistent.

Non-persistent Oils are refined oil products that will be completely removed from the affected environments through natural weathering processes. Only short-term impacts are expected from these refined products. In general, an oil is considered non-persistent if it requires days to weeks before natural weathering processes decrease the volume of the oil to half its original volume.

Residuals (or residue) are compounds left when crude oils are processed at refineries for the extraction of gasoline, diesel fuel, and other oil products. Residue is often blended with lighter-weight refined products for the development of residual fuels (often referred to as **Low API Gravity Oils** (LAPIO), or Group V oils) that are sold to utilities for the generation of electricity (Scholz et al., 1994).

Table 1. Persistence as defined by US 33 CFR, Section 155.1029.

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.

Purpose of Part II

- To discuss chemical dispersants and to answer the following questions:
 - what are they?
 - how do they work?
 - why would you want to use them?
 - what happens to the chemical dispersant once it is applied to the oil?
 - what are the differences/similarities between chemical dispersants and natural dispersion and dissolution weathering processes?

Surfactants are naturally occurring and chemically manufactured molecules often referred to as surface active agents or "detergents." Surfactant molecules contain both water compatible (hydrophilic) and oil compatible (oleophilic 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.

Solvents are chemical compounds that are included in dispersants to assist the surfactants in penetrating the oil.

Oleophilic refers to a chemical structure which has an affinity or attraction for oil or oil-like substances.

Hydrophilic refers to a chemical structure which has an affinity or attraction for water; these substances naturally repel oil and oil-like substances.

fined oils, etc. There are also several naturally occurring crude oils that are considered low API gravity oil products (Scholz *et al.*, 1994).

PART II: CHEMICAL DISPERSANTS

SECTION I: WHAT ARE THEY?

Chemical dispersants are mixtures that contain "surface-active" chemicals (SURFACTANTS) and SOLVENT(s). It is the surfactants that actually cause the oil to "disperse" into tiny droplets that remain suspended in the water column due to wave action. The molecules in surfactants are double ended, with one end having an affinity for oil (OLEOPHILIC) and the other an affinity for water (HYDROPHILIC) (NRC, 1989; Canevari, 1978) (Figure 1). The surfactant molecule attaches itself to an oil droplet with the oleophilic end while the hydrophilic end remains outside, on the surface of the oil where it adheres to water and repels other oil droplets. Once the dispersant is applied to the spilled oil on the water, the surfactants enhance the formation of oil droplets and reduce the oil's tendency to stick to other droplets or surfaces (e.g., beaches, animals, etc.).

Historically, the first large scale use of "dispersants" to clean oil spilled in the environment occurred in 1967 and involved heavy-duty detergent and/or degreaser solutions (refer to page 12 for more information); the detergents used were developed to clean oily residue on machinery, boiler rooms, workshop floors, and tanker compartments. These early "dispersants" were a mixture of toxic solvents and surfactants, but were effective in cleaning. The solvent was used to penetrate the oil (which could have become hardened by age or heat, or be mixed with a variety of other substances) and the surfactant was included to keep the now-softened oil suspended as an emulsion in the water used for cleaning. No one really worried about the relative toxicity of the solvents or the natural removal of the surfactants from the environment as they were not meant to be used directly in the environment (Lindblom, 1978; Lewis and Aurand, 1997). Use of these products in the 1967 *Torrey Canyon* spill was unfortunate and led to more damage than if they had not been used.

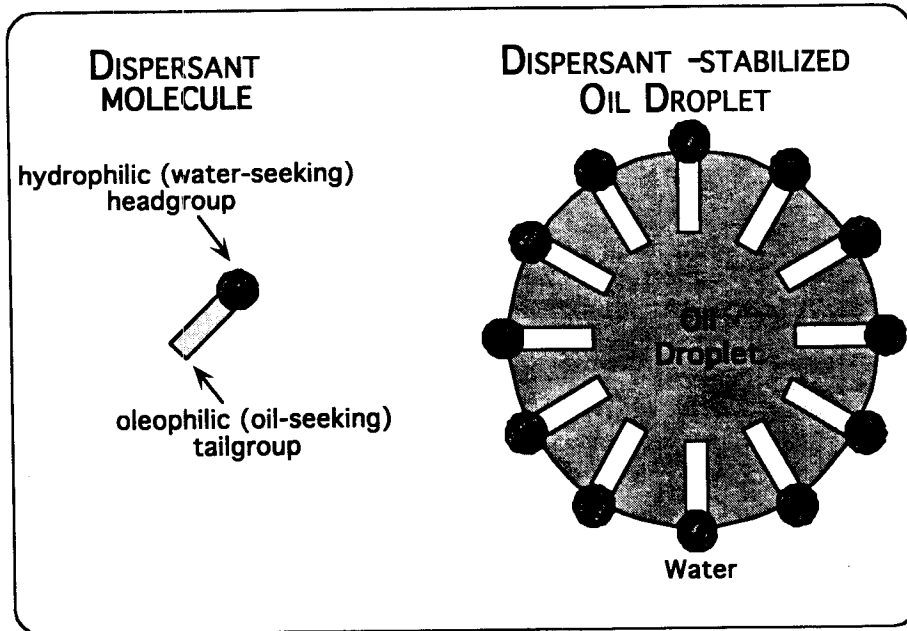


Table 2. Dispersants listed on the NCP Product Schedule as of January 1999.

1. Corexit 9500
2. Corexit 9527
3. Mare Clean 200
4. NEOS AB 3000

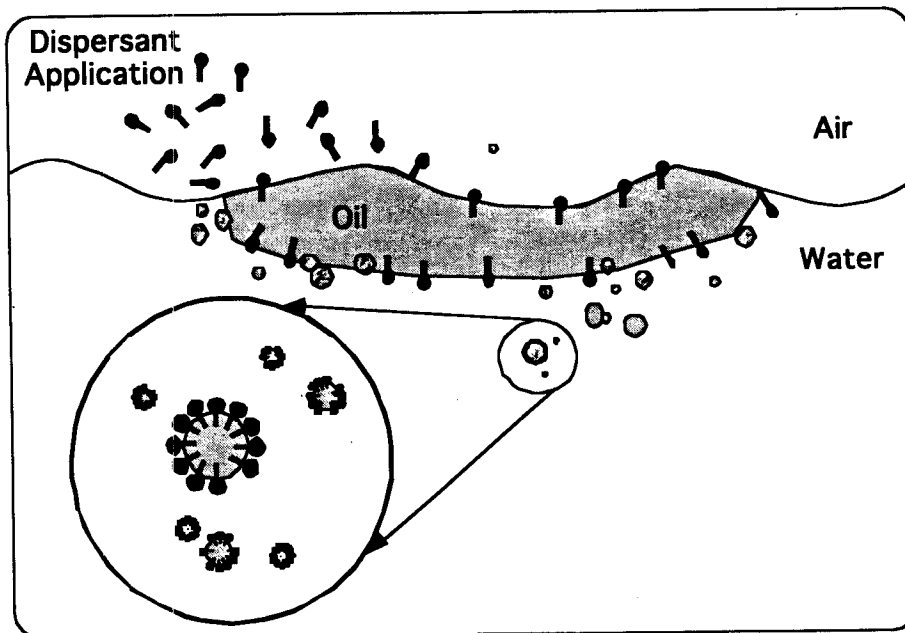


Figure 1. Surfactants and how they align themselves in oil. Adapted from IPIECA (1993).

Modern dispersant formulations are based on a mixture of solvents and surfactants but they are designed to be used in the environment to disperse oil with minimal toxic consequences. Dispersant formulations can be divided into three types, based on solvent classes involved in their manufacture (NRC, 1989; IPIECA, 1993; USEPA, 1998):

1. **water-based solvents** – dilutable with water for application; developed for use on light-distillate fuels and low-viscosity crude and products; least effective type;

**More on Modern
Dispersant Formulations**

PRODUCT	SOLVENT
Corexit 9500	Hydrocarbon-based
Corexit 9527	Hydrocarbon-based
Mare Clean 200	Solvent-based
NEOS AB 3000	Hydrocarbon-based

2. **hydrocarbon-based solvents** – enhances mixing and penetration of the surfactant into more viscous oils; usually used “neat” or undiluted, but can be diluted with water for application; the majority of dispersants fall under this category; and
3. **solvent-based containing lower concentrations of surfactants** (less than 20 to 25%) – only a limited number of these dispersants are in general use.

There are many familiar examples of surfactants available today for household use; however, they are not the same formulations as those surfactants found in chemical dispersants. Examples of these home products include, but are not limited to: Fantastik® and other all purpose grease cleaners; many types of glass cleaners; dishwashing soap; laundry pre-treatment products; and even some FDA-approved food additives. Solvents used in dispersants are found in many households, including turpentine, nail polish remover, and lighter fluid for cigarette lighters and BBQ grills.

Interfacial Tension is the SURFACE TENSION at the interface of two liquids or substances (Morris, 1992). Think of it as using soap to remove oil or grease off a shirt. Water alone cannot remove the stain; there is significant interfacial tension between the oil/grease and the water. However, adding soap (or surfactants) that has both water-loving and oil-loving components, loosens the oil/grease and suspends it in the water. The soap has broken the interfacial tension between the oil/grease and the water.

Surface Tension is the stretching force required to form a liquid film (Morris, 1992). This tension causes the water to bead up on surfaces, which slows wetting of these surface and inhibits the cleaning process. This can be seen by placing a drop of water onto a waxed car; the drop will hold its shape and will not spread because of surface tension.

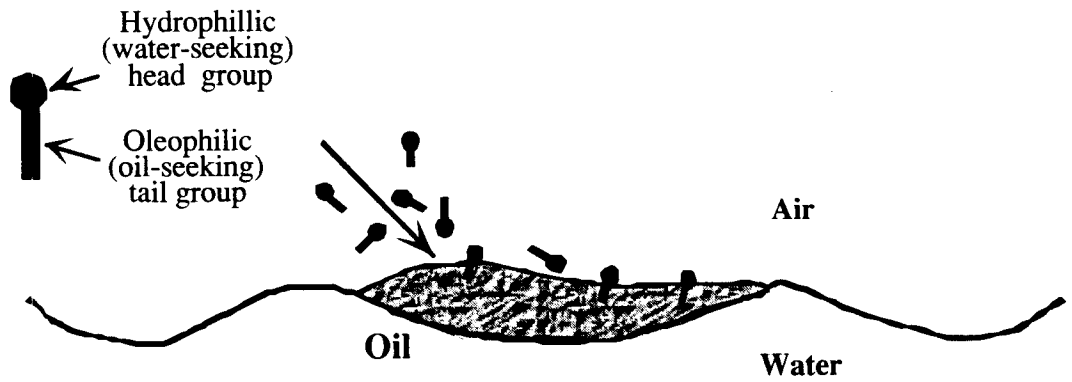
SECTION II: HOW DO CHEMICAL DISPERSANTS WORK?

Sea energy naturally mixes spilled oil into the water column. During periods of heavy wind and wave activity, the spilled oil will often get mixed into the water column, only to coalesce and resurface as a slick at a later time when the natural mixing forces have been reduced (calmer weather). An oil-spill dispersant properly applied to the spilled oil enhances the natural dispersion process. With surfactants, droplets are less likely to coalesce and produce large droplets which would rapidly resurface. Surfactants are the components in chemical dispersants that allow the oil slick to break into small droplets which more effectively mix into the water column and remain there until they are degraded by natural processes.

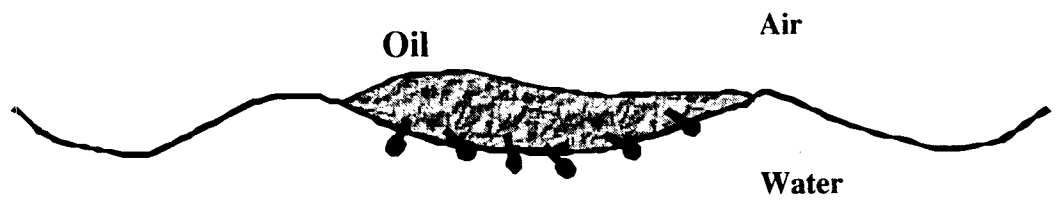
Canevari (1978; 1985) provides a brief, but concise summary of how the surfactant mechanism works (Figure 2).

“...dispersion occurs after the chemical dispersant penetrates the oil and settles at the interface of the oil and the water...When the surfactant arrives at the oil-water interface, there will be a dramatic reduction in the oil-water INTERFACIAL TENSION...there is a driving force for part of the [surfactant] to diffuse into the water...During this diffusion [of the surfactants into the water column], some oil associated with the surfactant as fine oil drop-

1. APPLICATION OF CHEMICAL DISPERSANT



2. SURFACTANT LOCATES AT OIL-WATER INTERFACE



3. OIL SLICK DISPERSES INTO DROPLETS WITH MINIMAL ENERGY

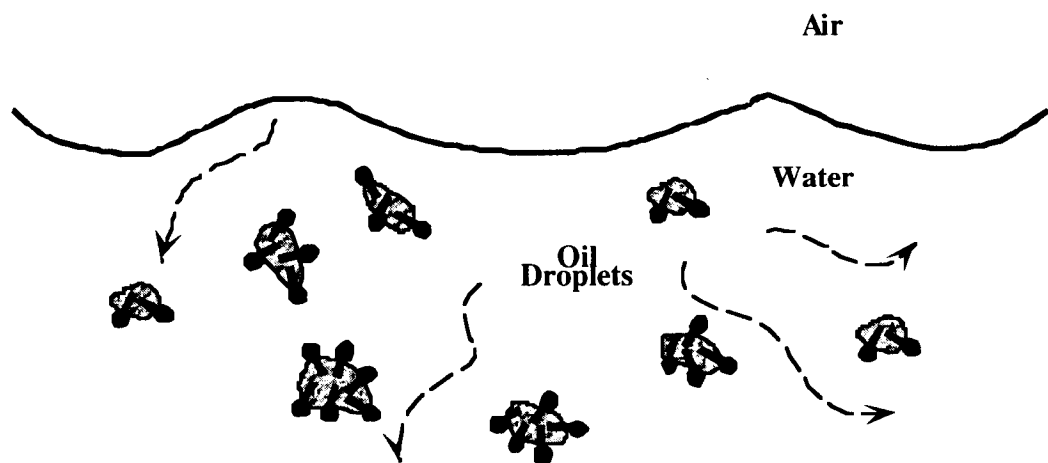


Figure 2. Mechanism of surfactant action in oil spilled on the water. Adapted from Canevari (1978).

lets is carried along with the surfactant into the water column.”

With the optimal application of the chemical dispersant to the surface slick, the surfactants will travel through the oil to the oil-water interface. Once there, even a low amount of wave or current energy can be sufficient to distribute the dispersant and encourage droplet formation. Some of the present-day dispersant formulations require little-to-no mixing energy to break the interfacial tension at the oil-water interface (Canevari *et al.*, 1989).

Chemical dispersants help prevent re-coalescence of the small oil droplets once they are formed. The surfactants remain at the oil-water interface of the chemically dispersed oil droplets long enough to act as a barrier between droplets which may collide with one another at random (NRC, 1989). Since chemically dispersed oil droplets are not prone to re-coalescing, the treated oil is unlikely to form tar balls and patties. Furthermore, these oil droplets have greater exposed surface area on a per volume basis relative to the original surface slick. This enhanced surface area can support a larger population of indigenous bacteria that naturally biodegrade the oil droplets.

SECTION III: WHY WOULD YOU WANT TO CONSIDER USE OF CHEMICAL DISPERSANTS?

During an oil spill response at sea, the primary objective is to minimize impacts from the spilled oil. The five most commonly considered responses to on-water oil spills are, in no particular order (Payne, 1994):

1. no response (i.e., no action or monitor only);
2. mechanical clean-up and physical removal;
3. the addition of chemical dispersant agents;
4. *in-situ* burning; and
5. bioremediation with nutrient or microbial additions.

There are various pros and cons associated with each (adapted from Payne, 1994):

- The **no response** option, or letting nature take its course (allowing the oil to naturally weather and break up) is usually a viable option when spills occur a great distance from shore or if prevailing winds are driving the oil away from shorelines and sensitive habitats. However, public perception of just leaving the oil alone to weather naturally may be politically unacceptable.

- **Mechanical clean-up and physical removal** options typically result in a 10-15 percent recovery rate at sea (IPIECA, 1993). This means that 85-90 percent of the spilled oil can remain in the environment or is physically altered by the natural WEATHERING processes affecting it (e.g., EVAPORATION, PHOTO-OXIDATION, BIODEGRADATION, SEDIMENTATION). Often mechanical recovery options are hampered by ambient conditions (e.g., currents greater than 1 KNOT and/or waves greater than 3 feet).
- **In-situ burning** has been estimated to be nearly 95 percent effective in removing oil contained within a fire-resistant boom on the waters' surface. However, the corralling of the oil for burning, using boats and towed boom, is subject to the same limitations (e.g., weather conditions) for mechanical removal. Previous on-water burn events resulted in concerns regarding the implementation of this technology, including: burn emissions (smoke), worker safety, and integrity of the spill source. *In-situ* burning is typically only viable for fresh oils that have not undergone much weathering, oils maintained in slicks that are 2 to 10 mm or greater in thickness, and oils that have not formed an EMULSION or that have an emulsion with less than 50 percent water incorporated (Buist *et al.*, 1994). Experienced personnel are required for proper deployment and maintenance of the fire-resistant boom during the burn.
- **Bioremediation** is a long-term clean-up option; it does not provide a "quick fix." Over long periods of time (months to tens of years), naturally occurring microbes will convert the remaining oil into its basic components: carbon dioxide and water. Bioremediation is considered a shore-based response option; it does not protect shorelines from getting oiled. To date, there have been no documented, scientifically valid, enhanced bioremediation programs using nutrient or microbial addition at sea (Payne, 1994). Public opinion often demands that pollution be taken care of immediately, forcing response personnel to forego this response option, except as a final "polishing tool" on shorelines.
- **Chemical dispersants** are designed to break up the surface slicks permanently, and disperse the oil as fine droplets into the water column so that the natural mixing action will dilute the subsurface oil concentration in the water column. This action transfers the oil from one location (the water surface) to another (spread out within the water column), where natural biodegradation can occur. Natural mixing forces dilute the concentration of oil dispersed into the water and therefore rapidly reduce any potential ACUTE (immediate) and CHRONIC (long-term) toxicity exposure to organisms through the

Weathering alters the physical and chemical properties of the spilled oil over time. Spilled oil and refined products are removed from the water's surface to the atmosphere, water column, sediments, and shorelines. This process is referred to as the "aging" of the oil.

Evaporation is the primary weathering process in the removal of the oil from the sea surface (dependent upon oil type). This loss physically changes the relative abundance of the oil components, often making these remaining materials more difficult to deal with during response operations.

Photo-oxidation is when components in oil are chemically transformed through a photo-chemical reaction (sunlight in the presence of oxygen) to produce new compounds which tend to be more water-soluble and toxic (in the short-term) than the parent compounds (Neff, 1990). This process plays only a minor role in the weathering of oil spilled on the water's surface.

Biodegradation is when naturally occurring bacteria and fungi consume petroleum hydrocarbons as a food source, transforming existing molecules into oxidized by-products that will eventually be further degraded through oxidation to carbon dioxide and water.

Sedimentation transfers oil from the surface and water column to the seafloor bottom through: 1) direct sinking; 2) adhering to suspended sediments that eventually settle-out; and 3) as fecal matter following ingestion.

A **Knot (Kt)** is a unit of speed equal to 1 nautical mile per hour, approximately 1.7 feet per second (51 centimeters per second or 1.15 mph).

Emulsions (water-in-oil) are formed when water is incorporated into the oil, forming a new product which is relatively resistant to other weathering processes (such as evaporation and dissolution). Emulsions are also referred to as "mousse" or "chocolate mousse" because of their color and visual appearance. Since water is being added to the oil, emulsification tends to increase the total volume of oily residue remaining in the environment, often by a factor of two to three.

Acute is used to define exposure or effect. Rand and Petrocelli (1985) define it as having a sudden onset, lasting a short time; of a stimulus, severe enough to induce a response rapidly (i.e., generally less than 4 days). Typical effects endpoints include mortality or immobility (DAC, 1996).

Chronic is used to define exposure or effect. Rand and Petrocelli (1985) define it as involving a stimulus that is lingering or continues for a long time; often signifies periods from several weeks to years (i.e., generally depending on the reproductive life cycle of the organism). Typical effects endpoints include reproductive, growth, or development impairment as well as behavioral changes (DAC, 1996).

environment. In several recent spills, dispersant application successfully prevented most or all of the oil from impacting shorelines which is the goal (Lewis and Aurand, 1997). In every case where spills have had major ecological impact, this has resulted from oil reaching the nearshore areas.

The NRC (1989) report on "Using Oil Spill Dispersants on the Sea" concluded that dispersion at sea, before a slick reaches a sensitive habitat (e.g., salt marshes, coral reefs, or mangroves), is considered a viable response technique as it can "reduce the overall and particularly the chronic impact of oil on many habitats....The principal biological benefit of dispersant use is the prevention of oil stranding on sensitive shorelines."

Several other reasons have been identified for the use of chemical dispersants in oil spill response. By removing oil from the water surface and diluting oil concentrations in the water column, chemical dispersion (NRC, 1989; IT Corporation, 1993; Lunel *et al.*, 1996):

1. reduces potential damage to birds, marine mammals, and other natural resources that could be impacted by oil on the water surface;
2. reduces the fouling of shorelines and other economically important resources (e.g., boats, marinas, shellfish beds);
3. provides a clean-up option when other response techniques are not effective (e.g., waves too high for booms and skimmers);
4. enhances microbial degradation by increasing the surface area of the oil droplets and exposing the droplets to these processes;
5. removes the oil from the action of the wind that may ultimately bring a slick ashore; and
6. reduces the formation of tar balls and mousse.

Dispersion does move the oil from the surface into the water column, potentially exposing water-column and nearshore shallow bottom-dwelling organisms to the oil. However, concentrations typically are low and drop very quickly, thereby minimizing impact. Exposure and impact considerations are the focus of the third booklet in this series "Defining the Links Between Fate and Transport Processes with Exposure and Effects of Oil and Chemically Dispersed Oil in the Environment."

SECTION IV: WHAT HAPPENS TO CHEMICAL DISPERSANTS ONCE APPLIED TO THE OIL?

What happens to the chemicals and the oil over time? Will they remain in their initial forms as a long-term source of pollution? or, Will the dispersant/oil droplet separate out over time and both become a long-term source of pollution?

Through the mixing energy provided by wind, waves, and currents, the chemically dispersed oil droplets will be rapidly distributed into the upper ten meters of the water column and remain dispersed in the water column. If they are small enough [generally less than 10-20 μm or 0.01-0.02 mm diameter; Lunel (1996) reports 70 μm or 0.07 mm in diameter], these oil droplets will remain dispersed in the water column due to natural currents or water column mixing, thus preventing the oil rising and reforming surface slicks. Once in the water column, the chemically dispersed oil droplets do not remain suspended permanently; both the chemical dispersant and the oil droplets undergo weathering similar to the oil on the water surface (i.e., dissolution, diffusion, biodegradation). Sedimentation of chemically dispersed oil droplets does not occur (Wilson and Putnam, 1982) and NRC (1989) reports that "chemical dispersion of oil leads to reduced interaction with suspended particulate matter or sedimentation." Furthermore, dispersed oil droplets do not undergo emulsification (Canevari, pers. comm.). The chemical composition of dispersed oil droplets will be approximately the same as the surface oil (with the exception of trace quantities of surfactants) (Payne, 1994).

For some dispersants, much of the solvent fraction of the dispersant can evaporate during and immediately after application to the oil. In present-day dispersant mixtures, solvents are added to dissolve surfactant and reduce viscosity so that the dispersant can be sprayed uniformly (NRC, 1989). The surfactant portion of the dispersant typically leaches out of the oil droplet over time (Neff, 1990; Payne, 1994) where it is readily degraded by bacteria and fungi and accumulated and metabolized by a number of organisms, like fish and plankton. However, injuries may result if organisms that are unable to metabolize these surfactants consume them. Metabolism of the surfactant by bacteria and fungi as well as fish and plankton is fairly complete, meaning that the surfactant is fully digested and broken down and is no longer biologically available (NRC, 1989).

Historically, initial dispersed oil concentrations in the water column have been reported in the range of 20 to 50 mg/L (PPM) for both actual spill

*A **Micron (μm)** is a unit of measurement; one μm is one-millionth of a meter. Fifty, 10- μm particles in a group (500 μm or 0.5 mm) would be approximately the size of the period at the end of this sentence.*

***PPM (parts-per-million)** is a unit of concentration. One ppm can be approximated by one teaspoon in 1,300 gallons.*

events and controlled studies when chemical dispersants were applied (Payne, 1994). These values are typically for the upper meter of the water column. With natural mixing within the water column, these values would be greatest directly under the slick and would diminish with depth and distance from the oil source (NRC, 1989).

WHY THE BAD REPUTATION? The *Torrey Canyon* Disaster

Historically, the bad reputation began when "degreasing agents" were used by the British government following the wreck of the *Torrey Canyon* in 1967. Many prime holiday beaches were impacted as 95,000 tons (593,750 barrels) of oil was released into the ocean. As part of the response, 10,000 tons (66,000 barrels) of chemicals were used to remove the estimated 14,000 tons (87,500 barrels) of weathered oil that impacted the shorelines in Cornwall, England (Southward and Southward, 1978).

These chemicals, although often referred to as "dispersants," were actually degreasing agents, formulated to clean ship bilges. They contained over 60 percent aromatic solvents (Lewis and Aurand, 1997) and both the solvents and the surfactants in these degreasing agents were highly toxic to marine life. Modern day dispersants are very different formulations from those chemicals applied during the *Torrey Canyon* spill. They are specifically designed for application to oil spills and pose a far lower risk to the environment. This is an important point that is often overlooked.

According to Nelson-Smith (1978), during the *Torrey Canyon* spill, [chemicals] "were applied from watering cans and buckets; full 45-gallon drums were perforated crudely and rolled over cliffs or dropped from helicopters in the general direction of the approaching slick. Inaccessible coves were treated by pouring the [chemical] mixture into streams a considerable distance inland from the polluted waterline. Beaches were sprayed regardless of whether they were of bedrock, shingle, or fine sand, often on a falling tide and without further washing." Compounded by the oil's natural ability to produce an emulsion or "chocolate mousse" that contained up to 80 percent water, the cleanup operation was greatly hampered by the highly viscous oil which floated on the water and clung to solid surfaces, smothering birds and other wildlife. The result of this haphazard use of degreasing agent use was an almost complete annihilation of all living animals and plants in many of the treated areas.

Although the use of degreasing agents during the *Torrey Canyon* spill was considered an environmental disaster, the United Kingdom now uses the newer dispersant formulations regularly as a part of its spill response efforts.

SECTION V: CHEMICAL DISPERSION VERSUS NATURAL DISPERSION AND DISSOLUTION

Natural dispersion and dissolution are weathering processes. Natural dispersion is the process of forming oil droplets (of the "WHOLE OIL") of various sizes that are incorporated into the water column in the form of a dilute oil-in-water suspension. Dissolution is the transfer of the individual components (not the whole oil) from the slick into solution in the water. Natural dispersion reaches a maximum approximately 10 hours following a spill, but may continue for several weeks. Dissolution typically occurs during the first 24 hours of a spill, reaching peak concentrations of dissolved compounds 8 to 12 hours after the initial release of the oil to the water surface (Exxon, 1985; Neff, 1990).

For a more detailed discussion of the natural dispersion and dissolution weathering processes, see the first booklet in this series, "Fate of Spilled Oil in Marine Waters: Where Does It Go, What Does It Do, and How Do Dispersants Affect It?"

Whole Oil is a reference to the oil itself, as a complex product. When referring to "whole oil," we are 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.

HOW DOES NATURAL DISPERSION COMPARE TO CHEMICAL DISPERSION?

SIMILARITIES

- Both cause small oil droplets to be dispersed into the water column; however, dispersants result in more and smaller droplets (reference).
- Both reduce the volume of the slick at the surface but do not change the physicochemical properties of the oil.
- Both increase the surface area of the oil, allowing for enhanced dissolution and enhanced microbial degradation.
- Both increase the oil's potential for direct interaction with particulate material because the oil is mixed into the water column. However, with a chemical dispersant, there is less attachment.
- Both make the oil more bioavailable to organisms living and feeding in the water column.
- Both produce decreasing concentrations of oil at increasing depths in the water column, due to natural mixing forces.

DIFFERENCES

- Evaporation of C1 to C10 components (the lighter hydrocarbons) occurs faster with chemical dispersion (API, 1986).
- Evaporation of the lighter components can increase fire and explosion hazards.
- Chemical dispersion results in a greater number of smaller droplets.
- Chemical dispersion prevents larger oil droplets from reforming at the surface. Natural dispersion does not.
- Chemical dispersion requires less mixing energy than natural dispersion (a wave height of a few inches versus a foot or more).
- Oil concentrations directly under the slick can be the same or higher (see below) with chemical dispersion as compared with natural dispersion depending on site-specific conditions (e.g., sea state, oil type, etc.). However, the concentrations of oil under the slick are rapidly diluted over time for both chemical and natural dispersion.
- Chemical dispersion stabilizes the oil droplet's oil-water interface, potentially reducing the oil's adhesion/attraction for suspended solid particles, feathers, and fur, which in turn reduces the amount of oil that could potentially sink or be available for injury. Natural dispersion does not reduce/inhibit the oil's adhesion to solid particles, feathers, or fur.
- Concentrations of oil dispersed under surface slicks are typically greater when chemical dispersants are applied than if left to naturally disperse. Naturally dispersed oil under surface slicks have been measured to reach 5–10 ppm (during the *Ixtoc-I* blowout; unusually high natural dispersion rates occurred because the source originated subsurface), but are typically only in the 100–500 PPB (0.1–0.5 ppm) range for the upper three meters of the water column for freshly spilled and/or released oils. These concentrations decrease with increasing depth due to water column dilution and natural mixing. In comparison, oil concentrations immediately (1 to 3 meters; API, 1986) under surface slicks that have been chemically treated range from 20–50 ppm (5 to 51 minutes after spraying; API, 1986) for spills of opportunity and controlled oil spills (Payne, 1994). The chemically dispersed concentrations in the water column are greater than values for naturally dispersed oils, often by a factor of up to 40 or more. As there is a greater concentration of chemically dispersed oil in the

PPB (parts-per-billion) is a unit of concentration. One ppm can be approximated by one teaspoon in 1,300,000 gallons (DAC, 1996).

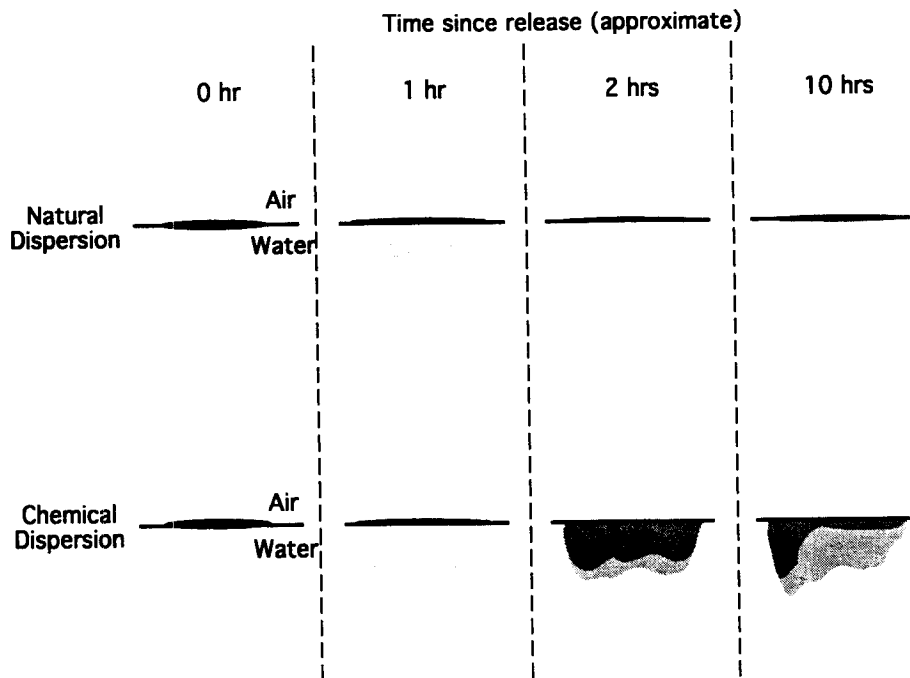


Figure 3. Comparison of the relative oil concentrations of oil droplets into the water column over time resulting from natural dispersion and chemical dispersion. Taken from IMO/UNEP (1982). Figure assumes no currents are present to mix the oil.

upper water column, natural mixing forces tends to mix more of the chemically dispersed oil deeper into the water column than untreated oil just undergoing natural dispersion (Figure 3).

HOW DOES DISSOLUTION COMPARE TO CHEMICAL DISPERSION?

SIMILARITIES

- Both dissolution and dispersion processes expose water-column organisms to the oil.

DIFFERENCES

- Dissolution transfers individual components of the oil into the water column; dispersion transfers the oil (as “whole” oil droplets) into the water column.
- Dissolved components eventually evaporate into the atmosphere, effectively removing these components from the water column.
- Dispersion results in oil entering the water column where it remains bioavailable; dispersion also creates greater surface area of the whole oil, resulting in increased dissolution and ultimately evaporation of the lighter-end components.

- Dispersion is a much more significant process than dissolution because it affects more of the spilled oil (by volume), over longer periods of time. Water column concentrations of dissolved crude oils are considered minimal; often in the ppm range.

SECTION VI: DISPERSANTS, SUMMARIZED

Modern dispersant formulations were developed to disperse oil into the water column quickly. In most cases, this is preferable to having untreated oil strand on shorelines. Because diffusion occurs in all directions due to natural mixing within the water column, the level of exposure is generally restricted to a short time period in a very finite area directly beneath the treated slick. Dispersants greatly reduce the potential for those organisms that are associated with the water surface to receive an acute or chronic exposure to the toxic portions of the oil. In contrast, undispersed oil can remain on the water surface or shoreline, exposing surface organisms to potentially higher concentrations of the oil over a longer period of time, and ultimately can cause high mortality if it comes ashore.

Wind, currents, and wave action provide the necessary energy to form dispersions of the oil in water. The addition of properly applied chemical dispersants reduces the energy required to break a slick into droplets, with chemically-aided dispersion potentially occurring even in the absence of breaking waves (wind speeds of ≤ 10 knots) (NRC, 1989).

As the dispersed oil mixes downward in the water column, oil concentrations beneath the treated slick decrease with increasing water depth because the oil droplets continue to be diluted into an increasing volume of water (refer to Figure 3).

As with many response options, there are trade-offs/issues that decision-makers must consider when dispersants are recommended for use:

1. Is the potential injury to water column and bottom-dwelling organisms acceptable if chemical dispersants are used to move the oil from the water surface into the water column (relative to impacts to surface resources if left untreated)?
2. Does the addition of chemical dispersants pose more or less of a hazard than the untreated oil to organisms existing in the habitat?

3. What is the window of opportunity for dispersant application? Regional, state, and local government involvement may inhibit the approval process to the extent that the window of opportunity is lost.
4. Are experienced, trained personnel available for an effective application?
5. Are ambient conditions conducive to dispersant use (e.g., minimal wind and wave height requirements) to provide the proper mixing energy? Are conditions expected to change?
6. Scientists and decision-makers may have different opinions/ understanding regarding the effectiveness and toxicity of chemical dispersants.
7. The use of chemical dispersants does not preclude the use of other conventional response techniques on the remainder of the untreated oil. Dispersants may be used in concert with other clean-up options.

PART III: OPERATIONAL ISSUES FOR CHEMICAL DISPERSANT USE

SECTION I: PRE-SPILL PLANNING FOR DISPERSANT APPLICATION

Because of the fairly short window of opportunity for dispersant application (up to 24 to 72 hours following an instantaneous release; Pond *et al.*, 1997b), at the time of an event, it is usually not possible to make a decision on their use unless some pre-spill planning has occurred. Regional, Area, and Local Response Teams should conduct a NET ENVIRONMENTAL BENEFIT ANALYSIS (NEBA), using an ECOLOGICAL RISK ASSESSMENT approach or similar detailed general evaluations, to determine the feasibility of using dispersants in a particular environment. There are some spill-specific conditions (e.g., weather, time of day, type of oil spilled, etc.) that will influence the decision to use dispersants. These are discussed in detail in the next section. However, there is preliminary information that can be gathered and examined to help in the dispersant planning process. As is evident from the

Purpose of Part III

- To discuss the need for pre-spill planning in order to facilitate actual spill response decision-making.
- To discuss the incident-specific considerations that need to be identified when considering the use of chemical dispersants.
- To review the application rates and equipment being used when applying chemical dispersants in the US.
- To discuss the need for a chemical dispersant monitoring program following an actual dispersant application.
- To provide a review of the current status of dispersant-use pre-approval in the US by coastal regions.

A **Net Environmental Benefit Analysis (NEBA)** is a process during which advantages and disadvantages of a proposed action are compared and weighed with reference to the ecological value and human use of environmental resources (Baker, 1997).

An **Ecological Risk Assessment** uses a defined methodology to determine effects from quantitative data. Information is incorporated into conceptual models and is interpreted against defined endpoints related to the protection of resources.

discussion below, many of the steps involved in a NEBA, especially when following a prescribed risk assessment approach, take time to complete. This is time that is not available during a response when a decision to use dispersants must be made fairly quickly.

Baker (1997) discusses the five steps involved in a NEBA:

- collect information on ecology, physical characteristics, and human use of environmental resources of the area proposed for cleanup, and details of the proposed cleanup method;
- review previous spill case histories and experimental results that are relevant to the area and cleanup method;
- on the basis of previous experience, predict the likely environmental outcomes if the proposed cleanup method is used, and if the area is left for natural cleanup;
- compare the advantages and disadvantages of the proposed cleanup with those of natural cleanup (no action); and
- weigh advantages and disadvantages with reference to the ecological value and human use of environmental resources to arrive at the optimum cleanup response.

Baker states that all parties must realize that the optimum response often cannot avoid all disadvantages.

Lewis and Aurand (1997) discuss the use of an ecological risk assessment to integrate NEBA into the pre-spill planning process. The risk assessment approach uses a defined methodology with specific endpoints to focus on "...appropriate issues, help clarify misconceptions, and avoid the use of inappropriate data by forcing all participants to explain their concerns in at least a semi-quantitative manner" (Lewis and Aurand, 1997). The methodology involves three phases and thirteen steps. The first phase, problem formulation, includes the identification of:

- participants;
- ecological resources of concern;
- endpoints;
- response measures and scenarios to be evaluated; and
- the potential effects of the countermeasure alone, countermeasure in combination with the oil, and the oil alone.

The last step in this phase involves the development of a conceptual model of the ecosystems affected. The second phase is the analysis, where ecological effects and environmental data are characterized and exposure defined. Risk characterization, the final phase, estimates the

potential ecological effects, determines the optimal response based on endpoints, integrates the results into contingency plans, provides for periodic revision and review, and data collection during response. A more detailed discussion of risk assessment can be found in the third booklet in this series, "Defining the Links Between Fate and Transport Processes With Exposure and Effects of Oil and Chemically Dispersed Oil in the Environment."

SECTION II: INCIDENT-SPECIFIC CONSIDERATIONS FOR DISPERSANT APPLICATION

Before applying a dispersant the reader should consider a number of environmental, oil, and dispersant conditions, along with other constraints on his decision-making.

ENVIRONMENTAL

SEA STATE

The relative SEA STATE in the spill vicinity can assist or hinder a dispersant operation. A certain amount of turbulence (sea state of 1 to 5; Table 3) is generally required to activate the surfactant's ability to break up and disperse the surface oil slicks (Kucklick and Aurand, 1995). This mixing energy is required to mix the oil down into the water column so that the small oil droplets will disperse with the prevailing currents. In moderate to heavy seas, the wave action acts as a large blender, forcibly mixing the oil into the water column.

Sea state also plays a role in determining the application rate for a given spill volume. In general, the rougher the seas, the less dispersant is required to break up a surface slick.

SALINITY

Most dispersants in use today, and the four on the NCP Product Schedule, are formulated to work best in water of 30 to 40 PPT (Table 3), but dispersant effectiveness is also tied to the type of oil being dispersed as well as the receiving water's salinity. Testing has shown that many dispersants have decreased efficiency in freshwater (Fritz, 1995).

WATER TEMPERATURE

The main impact of water temperature is its affect on an oil's viscosity. Colder temperatures could increase the viscosity to the point where chemically dispersing the slick would be more difficult. Dispersants have been applied with good results in numerous cold water situations including laboratory tests, sea trials, and actual spill events. Research efforts continue.

Sea state is a numerical code that describes the height of wind-generated waves. It is often compared to the average wind speed generating those waves: e.g., a sea state value of 0 (1 to 3 knot winds = 0.4 ft. average wave height) to 9 (56 to 71 knot winds = 36 to > 47 ft. average wave height) (Bhahacharyya, 1978; Kucklick and Aurand, 1995).

Salinity is a measure of the quantity of dissolved solids in ocean water (measured in parts-per-thousand, ppt).

Parts-per-thousand (ppt; ‰) is a unit of metric measurement to express the concentration of dissolved solids in water.

Table 3. Salinity values for various water bodies.

Waterbody	Salinity (ppt)
Freshwater	0.0
Brackish	5.0 - 15.0
Ocean	32.0 - 35.0
Dead Sea	345.0

SEA		WIND			WAVE HEIGHT
Sea State	Description	(Beaufort) Wind Force	Description	Range (knots)	Average (ft)
0	Sea like a mirror	0	Calm	1	0
	Ripples with the appearance of scales; no foam events	1	Light airs	1-3	0.04
1	Small wavelets; short but pronounced crests have a glossy appearance, but do not break	2	Light breeze	4-6	0.3
	Large wavelets; crests begin to break; glossy in appearance	3	Gentle breeze	7-10	0.8 to 1.1
2	Small waves becoming larger	4	Moderate breeze	11-16	1.6 to 2.1
3	Small waves becoming larger; fairly frequent horses	4	Moderate breeze	11-16	2.3 to 2.9
4	Moderate waves, taking a more pronounced long form; many white horses formed (chance of some spray)	5	Fresh breeze	17-21	3.7 to 4.6
5	Large waves begin to form	6	Strong breeze	22-27	5.5 to 6.6
6	Large waves begin to form; wake crests are more extensive everywhere (probably some spray)	6	Strong breeze	22-27	6.8 to 7.7
7	Sea heaps up and white foam from breaking waves begin to be blown in streaks along the direction of the wind	7	Moderate gale	28-33	8.9 to 11.6
	Moderate high waves of greater length; edges of crests break into spindrift. The foam is blown in well-marked streaks along the direction of the wind. Spray affects visibility	8	Fresh gale	34-40	13.1 to 18.2
8	High waves. Dense streaks of foam along the direction of the wind. Sea begins to roll. Visibility affected. Very high waves with long overhanging crests	9	Strong gale	41-47	20.1 to 24.1
		10	Whole gale	48-55	26.2 to 33.2
9	Exceptionally high waves. Sea completely covered with patches of foam lying in direction of wind. Everywhere edges of wave crests are blown into froth. Visibility affected	11	Storm	56-63	35.7 to 40.3
	Air filled with foam and spray. Sea white with driving spray. Visibility very seriously affected	12	Hurricane	64-71	> 46.6

Table 4. Comparison and definitions of sea conditions (Bhahacharyya, 1978).

ECOSYSTEM

When considering chemical dispersants, the decision-maker often has to make environmental trade-offs (e.g., Is it better to protect the mangroves or the commercial fishing ground? Marine mammals or a bird rookery?). Water depth and proximity to shore are only two of the ecosystem considerations a decision-maker needs to be aware of when considering the use of dispersants. There is no generic right answer. Some planning in advance to prioritize all the resources at risk can be invaluable in making such judgments. A rapid risk assessment for each spill should be used to determine the best course of action regarding the use of dispersants.

OIL

CHEMICAL COMPOSITION

The chemical composition of an oil is an important factor in determining whether an oil is a candidate for chemical dispersion. Knowing an oil's API GRAVITY and POUR POINT helps the decision-maker assess an oil's relative dispersibility. As a rule of thumb, an oil with a high API gravity [$^{\circ}\text{API} \geq 45$ (a low viscosity oil)] does not need to be dispersed because the oil is non-persistent (e.g., gasoline, condensates) and will evaporate quickly (refer to Table 1). Oils with a very low API gravity, [$^{\circ}\text{API} \leq 17$, (high viscosity oils and oil products)] are not viewed as dispersible because these oils (e.g., very heavy No. 6 fuel oil, residual oils, heavy slurry oils) are so heavy that dispersants were considered ineffective, until recently. New advances in dispersant formulations are leading to products which are effective on heavy oils (DeMarco *et al.*, 1998). Oils with API gravities between 17 and 45 are generally considered dispersible, depending on the oil's pour point. Dispersion will not occur if the water temperature is below the pour point. This information, summarized in Table 5, is based on an American Petroleum Institute study that assessed the dispersibility of a number of crude and refined oils (John Yeager and Assoc., 1985).

Often, people want a list of what oils are dispersible. Table 5 lists representative examples of crude and refined oils and their dispersibility. Two documents, John G. Yeager and Assoc. (1985), and the Regional Response Team VI Preapproved Dispersant Use Manual (1995), provide much more extensive lists.

API Gravity is a scale for measuring fluid specific gravities (SG) 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 ($^{\circ}\text{API} = 62$); inversely, an oil with a high specific gravity (e.g., very heavy crudes; SG = 0.98) will have a low API gravity value ($^{\circ}\text{API} = 13$). SG = 1 is equivalent to an API gravity = 10.

$$\text{API gravity} = (141.5 / \text{SG}^*) - 131.5$$

* at 60 °F

Pour point is the temperature below which a liquid (in this case oil) will not flow.

DESCRIPTION	API GRAVITY (°)	CRUDE OIL EXAMPLES	REFINED PRODUCT EXAMPLES
Very light-weight material. No need to disperse. Oil will dissipate rapidly.	over 45	Algerian Blend	Gasoline Condensates, most Naptha
Light-weight material. Relatively non-persistent. Easily dispersed.	35 to 45 (Pour point under 41 °F)	Brent Ekofisk Forties Murban Seria Light	Diesel Fuel Jet Fuel Kerosene
Light-weight material. Relatively non-persistent. Probably difficult to disperse if water temperature is below pour point of material.	35-45 (Pour point over 41°F)	Ardjuna Beatrice Camar Lucina Palanca Angola Pennington	Unfinished oils
Medium-weight material. Fairly persistent. Easily dispersed if treated promptly.	17 to 34 (Pour point under 41 °F)	Alaskan Arabian Light Basrah Dubai Iranian Heavy Kuwaiti Maya Oriente	
Medium-weight material. Fairly persistent. Probably difficult to disperse if water temperature is below pour point of material	17 to 34 (Pour point over 41 °F)	Bonny Light Coban Blend Gamba LSWR Minas Santa Cruz Taching Zaire	
Probably difficult or impossible to disperse.	less than 17	BCF 22 Boscan Laguna Lagunillas Meray Pilon	Asphalt Lube Oil Paraffins/Waxes Residual Fuels

Table 5. Relative dispersibility categories for various crude oils and refined products, based on API Gravity values and pour point. Adapted from Yeager and Associates (1985).

DEGREE OF WEATHERING

The degree of weathering or “aging” that an oil has undergone affects its dispersibility. In general, a fresh oil is more easily dispersed than one that has been extensively weathered or has become emulsified. The degree of weathering and an oil’s viscosity are intimately tied. The longer an oil is on the water, the more weathering the oil undergoes. Weather-

ing removes the lighter components of an oil. As these lighter-weight components are removed, the chemical composition of the oil changes and the viscosity of the oil increases.

There is a window-of-opportunity for the use of dispersants that varies with oil type. Some oils very rapidly become difficult to treat, while others remain amenable to dispersion for much longer. Generally, the window-of-opportunity for effective dispersant application ranges up to 24 to 72 hours following an instantaneous release (Pond *et al.*, 1997b). New dispersant formulations have the potential to expand this range.

DISPERSANT

In the US, there are several factors to consider regarding the dispersant itself and its use.

- Is the chemical dispersant listed on the USEPA NCNational Product Schedule? If not, it cannot be used in US waters.
- Has dispersant pre-approval been authorized by the Regional Response Team (RRT)? If not, has the request for use been approved by all necessary RRT members?
- Is the chemical dispersant available? What quantity?
- Are the dispersant application equipment and personnel available?
- What are the proper application rates for this chemical dispersant? and, How much oil is contained in the slick being dispersed?
- Are experienced personnel in charge of the dispersant application?
- Is the oil in a cohesive slick that is optimal for dispersal? or, Have the ambient wind and wave conditions caused the formation of WINDROWS, which makes dispersant application more difficult?

Windrows are areas of a slick on the water under the influence of wind and currents; a series of thin parallel patches that align themselves parallel to the direction of the wind (Lewis and Aurand, 1997).

FOR MORE INFORMATION...

Dispersants have been applied in the US during actual oil spills eleven times in the past 30 years (Table 5). As of 1989, they have been applied only five times. In all but one instance, the spills were in the offshore marine environment.

Year	Name	General Location	Volume of Oil (gal)	Oil Type	Dispersant Used	Reported Effects
1969	<i>Florida, Barge</i>	Marine Nearshore	175,000	No. 2 Fuel Oil	?	Little to no effect on oil; severe shoreline impacts in marshes.
1969	Well A-21, Platform A (Santa Barbara)	Marine Nearshore	3.2 million	Santa Barbara Crude	ARA Gold Crew Bilge Cleaner	37,500 gal applied by aircraft. No estimate of effectiveness; no impacts attributed to its use.*
1970	<i>Delian Apollon</i>	Estuarine	?	No. 6 Fuel Oil	COREXIT 8666 and 7664	Used to restore tidal zones; revealed no additional impacts from dispersants.
1970	Chevron Main Pass Block 41	Marine Offshore	1.5-2.7 million	GOM Crude	Primarily COREXIT 7664	2,000 drums sprayed around platform. No evidence of effects on shrimp, blue crabs, or commercial fish.
1978	<i>Pennsylvania, Barge</i>	Marine Nearshore	37,000 and 6,000	No. 6 Fuel Oil and No. 2 Fuel Oil	COREXIT 9527	Effectively dispersed oil.
1984	<i>Puerto Rican</i>	Marine Offshore	4.2 million	Lube Oil/ Lube Oil Additives	COREXIT 9527	2,000 gal used to disperse slick moving towards shore. Judged to be effective.*
1987	<i>PacBaroness</i>	Marine Offshore	more than 1,200 gal per day	Possible Diesel	COREXIT 9527	200 gal applied by aircraft to leading edge of slick; appeared successful. 50 more applied by helicopter in test site near site of sinking; also effective.
1989	<i>Exxon Valdez, PWS, Alaska</i>	Marine Offshore	11 million	Alaska North Slope Crude	COREXIT 9527	Test application
1990	<i>Mega Borg, Gulf of Mexico</i>	Marine Offshore	12,000-40,000 (did not burn)	Light Crude	COREXIT 9527	Applied to 15-mile long slick offshore.
1995	West Cameron 198	Marine Offshore	21,000-30,000	Light, Natural Gas Condensate	?	
1997	VASTAR, Gulf of Mexico	Marine Offshore	4,800	Natural Gas Condensate	COREXIT 9500	1,800 gal applied by DC-4 6 hours after spill. Estimated that 70 percent of a 5 km ² slick was treated with a 60-80 percent effectiveness.
1998	Pipeline break, Coast of Texas	Marine Offshore	100,000	Medium Sweet Crude	COREXIT 9527	3,000 gal applied by DC-3 and DC-4 aircraft. Documented successful dispersion through USCG SROMP Team and fluorometry and visual observance.
1998	ULCC RED SEAGULL Gulf of Mexico	Marine Offshore	20,000	Arab Light Crude	COREXIT 9500	80 gal applied using tanker tender's fire monitor system. Documented successful dispersion through fluorometry readings.

*Results are considered questionable.

Table 6. Dispersant Use for Major Oil Spills in the United States, 1969-1998. Adapted from Lewis and Aurand, 1997 and information supplied by Exxon (1998).

SECTION III: APPLICATION RATES AND EQUIPMENT

APPLICATION RATES

Application rates are important; too much dispersant places excess chemicals into the water column, with no additional benefit to the surface slicks; too little, and the application may not be effective, as the interfacial tension at the oil-water interface may not be sufficiently reduced to disperse the oil droplets. The USEPA Product Schedule test procedure (40 CFR Part 300, Appendix C 2.5) uses a 1 to 10 ratio of dispersant-to-oil. A dispersant is considered effective if a test application results in at least a 45 percent dispersion of the oil in the laboratory. Furthermore, the Preamble to the 1994 Final National Contingency Plan (NCP) Federal Regulation states that a 1 to 10 dispersant-to-oil ratio is the expected maximum dispersant application rate for actual spill use.

As of 1997, the recommended chemical dispersant application is typically reported as a 1 to 20 dispersant-to-oil ratio based on several laboratory studies (Lewis and Aurand, 1997). In the field, higher dispersant-to-oil ratios may be being used (reaching the NCP guidelines of dispersant-to-oil ratios of 1 to 10) (ITOPF, 1987).

Dispersant use data from more recent spills show that the dispersant-to-oil ratio has been greatly reduced with new chemical dispersant formulations. During the *Sea Empress* spill off Great Britain in 1996, the dispersant-to-oil ratio was a little as 1 to 65, and during the *CAPTAIN* spill in Scotland (August 1997), the ratio was on average 1 to 80 (Lessard, pers. comm.). Furthermore, Mackay (1995) has shown dispersant effectiveness in both a wave basin study and lab testing with a dispersant-to-oil ratio ranging from 1 to 100 to as little as 1 to 300.

The dispersant application rate (the dispersant-to-oil ratio) is dependent upon the oil type, the extent of weathering the oil has already undergone, the dispersant used, and the weather/wave conditions at the application site. Light-weight, low viscosity oils or rough sea conditions would require less dispersant (1 to 50, 1 to 100, or even less) to break up a slick (Lunel, 1996). On the other end of the spectrum, high viscosity oils (e.g., bunker C or No. 6 fuel oils or crude oils that are waxy or have weathered into highly stable, high viscosity emulsions), oils nearing their pour point, or seas under relatively calm conditions may not disperse even when much higher treatment rates (such as 1 to 10 or more) are used (Lewis and Aurand, 1997).

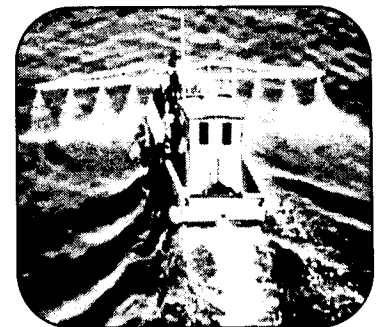


Photo Credit: NOAA, 1998

Figure 4. Vessel-Based Dispersant Application.

APPLICATION TECHNOLOGIES USED TODAY

Several application systems have proven to be effective in applying dispersants. These include (Lewis and Aurand, 1997; IPIECA, 1993):

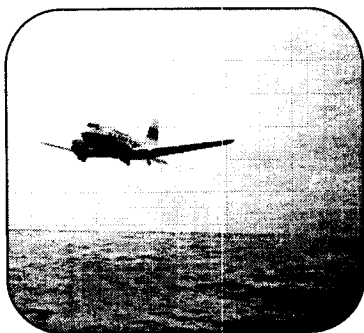


Figure 5. DC-3 Spraying Dispersant.



Figure 6. Helicopter Spraying Dispersant.

1. **Vessel-based systems** – These can be fitted to almost any boat/ship and are relatively inexpensive to use (Figure 4). Vessel-based systems: 1) are a good platform that can operate for prolonged periods; 2) can remain on site or travel with the slick; and 3) can store large quantities of dispersant on board. This method is most effective on small- and medium-sized fresh spills or polishing edges of large spills. However, being essentially at water level, boat-based applications require directions to the thicker portions of the slicks from spotter aircraft in order to be used effectively.
2. **Fixed-wing aircraft-based systems** – These systems allow a rapid response and quick treatment of large areas (Figure 5). There are several modified aircraft systems located around the United States that are available for dispersant application. In essence, this response option is limited in terms of the aircraft arriving on-scene and the time it takes to refuel and refill the application tanks. This method also requires considerable operational support including a trained spotter, and typically can be conducted only during daylight hours with relatively good visibility and flying conditions. At present, the largest plane can apply 5,000 gallons of dispersant per sortie.
3. **Helicopter-based systems** – These systems allow rapid response and relatively high coverage (Figure 6). They are a preferred option for small spills. Helicopters can be operated from land and on board large response vessels at sea, but the cost for use of the equipment is typically greater than fixed-wing aircraft. Dispersant operations using helicopters can be conducted only during daylight hours with relatively good visibility and flying conditions.

All of these technologies require trained and skilled personnel for use.

In the US, one of the issues regarding dispersant use revolves around chemical and equipment stockpiling. Because of a lack of proper incentives for dispersant use, stockpiles of dispersants and delivery systems are not readily available in many locations. Stockpiles of chemical dispersants and application equipment need only be located centrally because they are considered relatively mobile via aircraft. There are various groups, both public and private, that have established oil spill response capability, including the use and application of chemical dis-

persants; most are found in areas where spills are most likely to occur. The US Coast Guard (USCG) maintains response equipment at 19 sites around the country to supplement private efforts; however, only a few are equipped for chemical dispersant applications. The US Navy Superintendent of Salvage maintains a large fleet of pollution response vessels and specialized response and vessel-salvage equipment, primarily for Navy use, but they are available for response to any emergency when requested by the USCG. The USCG and US Air Force train personnel and equip C-130 aircraft for dispersant applications. Industry is contracting with private companies that provide both smaller and larger craft for dispersant applications.

As regions, areas, and industry progress from developing pre-authorization agreements to implementing them, stockpiling and application platform issues will continue to be addressed.

SECTION IV: CHEMICAL DISPERSANT MONITORING

Once dispersant application has commenced, it is valuable to monitor the application to determine if:

1. the dispersant was applied at the appropriate dosage in the correct locations;
2. the dispersant is working effectively; and
3. there are any obvious (qualitative) ecological effects (Pond *et al.*, 1997b).

Monitoring is also used to improve future dispersant use decision-making through long-term data gathering. Operational monitoring (monitoring during the dispersant application), is a qualitative process, involving visual observations by trained personnel. Decision-makers need to be briefed on the efficacy of the operation, so they can make informed decisions on whether or not to continue using a specific response option (i.e., chemical dispersants). Oftentimes, dispersion may not be instantaneous and visible changes to the slick may not be apparent for several hours; dispersion may be occurring but hidden by a thick film of undispersed oil above it. This makes it more difficult to determine effectiveness visually. Sometimes, visual observations are supplemented with fluorometry. A FLUOROMETER is employed to determine oil concentrations under slicks in the water column, as a technical aid for determining dispersant effectiveness. "Fluorometry readings can provide a qualitative measure of dispersant effectiveness if readings are

*A **Fluorometer** is an electronic measuring device which has a remote detection system that can be towed through the water while continuously recording fluorescence emitted due to the presence of turbidity, chlorophyll, certain components of oil, etc. The fluorometer only samples for the water soluble aromatic hydrocarbons, rather than for whole oil. Fluorometry provides qualitative, rather than quantitative measurements because it does not provide a reliable, real-time estimate of the quantity of oil in the water column (Pond *et al.*, 1997b).*

taken both under the dispersed slick and under an untreated portion of the spill, and then the results are compared. However, the temptation exists to extrapolate from those readings an estimate of the environmental effects based on the quantity of oil encountered and the chemical constituents of the spilled oil” (Pond *et al.*, 1997b). This cannot be done primarily because fluorometry offers little indication of the chemical composition of the dispersed oil.

SECTION V: CURRENT STATUS OF DISPERSANT PRE-APPROVAL IN THE US

The 1994 revision to the NCP (40 Code of Federal Regulations 300), Subpart J, requires decision-makers to engage in dispersant consultation and concurrence as part of their contingency planning process. As a result of this mandate and a number of educational outreach efforts and summary reports, many coastal Regional Response Teams have established pre-authorization agreements for dispersant use. As of December, 1998, seven of the nine coastal regions have established pre-authorization for dispersant use in specified areas. Table 7 summarizes the status and pre-approval zones for the coastal regions.

SECTION VI: DISPERSANT OPERATIONS, SUMMARIZED

Operational issues associated with dispersant use include not only how to apply the dispersant (i.e., by vessel, fixed-wing aircraft, or helicopter) but in what quantity and at what rate. Typically, the recommended chemical dispersant-to-oil application ratios range from 1 to 10 to as little as 1 to 300, although this is dependent on site-specific conditions, primarily the type of oil spilled and the weather conditions.

Operational issues also include concerns about applying the dispersant in the first place. These issues can and should be considered prior to the spill event. Pre-planning activities are essential in order to realistically receive the approval for dispersant use during an optimum window of opportunity: typically 24 to 72 hours following a spill. Other considerations cannot be dealt with until the spill occurs. Environmental conditions (sea state, salinity, water temperature, and ecosystem), oil properties (chemical composition and degree of weathering), and the dispersant itself are all issues that must be addressed at the time of the spill but prior to dispersant application.

Coastal Region	Status	Zones
I Maine New Hampshire Massachusetts Rhode Island Connecticut	Pre-approved in ME, NH (ME Area committee), MA, and RI (MA Area Committee). CT is not part of either agreement.	FOSC and state OSC discretion >2 nmiles from shore. Consultation with trustees required between 0.5 nmiles and 2 nmiles from shore. <0.5 nmiles from shore case-by-case.
II New York New Jersey	Pre-approved	Pre-approval at discretion of the FOSC, >3 nmiles offshore along the entire coast of NJ and along the south shore of Long Island (NY). A trial application of dispersants can be conducted in areas >0.5 nmiles excluding bays and coves.
III Delaware Maryland Virginia	Pre-approved	FOSC discretion >3 nmiles from shore and for test application >0.5 nmiles from shore.
IV North Carolina South Carolina Georgia Florida Alabama Mississippi	Pre-approved	At the discretion of the FOSC, >3 nmiles from shore and >33 ft water depth, except in special federal management areas, designated exclusion areas, and in FL where water depth must be 65 ft.
VI Louisiana Texas	Pre-approved	At the discretion of the FOSC, >3 nmiles from shore and >33 ft water depth.
IX California	Expedited; enhanced quick approval zone for offshore waters	Enhanced quick approval zone is 60ft or 0.5 nmiles offshore, whichever is more restrictive, with exceptions around kelp beds and mouths of anadromous fish streams. Concurrence of state, EPA, DOI, and DOC is still required but can be obtained through a single conference call.
X Oregon Washington	Case-by-case	The state final EIS outlines specific dispersant use categories based on geographical location and location of sensitive resources. It includes a rather complex evaluation of offshore areas, dividing them into more than 100 discrete blocks, in each of which pre-approval may or may not exist at any given moment (depending on time of year, weather conditions, etc.).
X Alaska	Pre-approved in Zone 1	Established three dispersant use zones based on physical and biological parameters, human use activities, and time to respond.. Zone 1 acceptable; at FOSC discretion. Zone 2 = conditional; requires consult with RRT and approval of EPA and State and continuous monitoring. Zone 3 = not recommended - case-by-case basis; requires consult with RRT and approval of EPA and State and continuous monitoring
Oceania Hawaii only	Expedited	FOSC in consultation with RRT representatives of the EPA, USFWS, NMFS, and the Department of Land and natural Resources through the State of Hawaii department of health for offshore areas >60ft in depth
Caribbean Puerto Rico US Virgin Islands	Pre-approved	Puerto Rico: at the discretion of the FOSC, \geq 0.5 nmiles offshore and >60 ft in depth. US Virgin Island: at the discretion of the FOSC, >1 nmiles offshore or 1 nmiles from coral reef (that is < 20 ft from surface) and > 60 ft in depth.

Table 7. A summary of dispersant pre-authorization, as of December 1998, by RRT Region.

Finally, once dispersants are applied, operational monitoring activities should occur to qualitatively evaluate the effectiveness of the dispersant's application and to identify any obvious ecological effects. Long-term monitoring of ecological effects can also be used to improve future dispersant decision-making. A more detailed discussion of long-term monitoring can be found in the third booklet in this series, "Defining the Links Between Fate and Transport Processes With Exposure and Effects of Oil and Chemically Dispersed Oil in the Environment."

IN SUMMARY...

Oils are composed of various quantities of light-, medium-, and heavy-weight hydrocarbons, with some asphaltenes, waxes, and trace chemicals. Every oil will disperse differently depending on its characteristics. Chemical dispersants are surfactants, with solvents added for application and to promote penetration of the surfactants to the oil-water interface. Surfactants attach to both the oil and water, enhancing formation of small droplets of oil into the water, thereby dispersing the oil. Both natural and chemical dispersion remove oil from the water's surface and increase the total surface area of the oil by forming droplets.

Chemical dispersants can prevent injury to animals and shorelines by enhancing natural dispersion. Chemical dispersants also increase oil concentrations directly under the slick and prevent re-coalescence of larger droplets at the surface. These concentrations are rapidly diluted.

Best considered for spills in sea states of 2 - 5, and during the first 24 to 72 hours following a spill, dispersants are most effective on light- to medium-weight oil of API gravity between 17 and 45 (oils with API gravity values higher than 45 do not need to be dispersed as they are rapidly removed from the water surface through natural weathering processes; oil with API gravity less than 17 typically do not disperse). Four dispersants are presently listed on the NCP Product schedule signifying that the manufacturers have completed the necessary information requirements for listing. Being listed on the NCP Product schedule does not mean that the product is recommended, approved, or authorized for use, just that the data requirements for submission have been completed. Pre-approval, availability of dispersant application equipment and experienced personnel, and the size and shape of the spill should all be considered in making a dispersant application decision. Monitoring can be done visually or with fluorometry; dispersion can be slow and is not always immediately visible.

The US National Research Council recommends that dispersants be considered along with other options as a first line of defense against spills. However, for dispersants to be a viable response option, formal approval should be requested immediately after the spill and supply/application logistics should be initiated as soon as practical. Dispersants can be used in concert with more traditional cleanup response activities.

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