

ExxonMobil Oil Spill Dispersant Guidelines



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This guidance document is intended for use by ExxonMobil employees and contractors who are trained in the use of oil spill dispersants. The information presented has been selected from many sources as of August 2007 and condensed to present concise recommendations that reflect the authors' best professional judgment concerning strategies for the use of these dispersants. Safety, health, and environmental regulations and related legal issues applicable to dispersants and dispersant activities are not addressed in this document. This document is not a substitute for and should not be relied upon in place of appropriate training, timely technical advice, or common sense.

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DEDICATION TO EXXONMOBIL EMPLOYEES WHO HAVE CONTRIBUTED TO DISPERSANT TECHNOLOGY

ExxonMobil has been involved with dispersant research since the 1960s, having initiated a development program following the 1967 *Torrey Canyon* spill off the UK Cornish Coast. At the time of the *Torrey Canyon*, there were no specially-formulated products for the dispersion of oil into the marine environment, and degreasing agents high in aromatic compounds were employed to clean the UK beaches. Those products had the potential to cause major ecological impacts of their own and demonstrated a clear need for low-toxicity agents formulated specifically for dispersing oil into the marine environment. This led Jerry Canevari of Standard Oil of New Jersey (one of the predecessors to Exxon Mobil Corporation) to formulate the first dispersant product intended for safe use in the marine environment. Starting with this new product and continuing to this day, numerous ExxonMobil scientists have made contributions to the field of oil spill dispersion through 40 years of research studies on new and better ways to mitigate the effects of oil spills through application of dispersants. Although we do not wish to minimize the contributions and impacts of many other engineers/scientists/researchers from other institutions and agencies worldwide who have also been part of this history, it is to the following group of committed ExxonMobil professionals that we dedicate this Manual.

The two primary ExxonMobil contributors are:

Jerry Canevari: pioneer who formulated most of the COREXIT line of dispersants, including self-mix products specifically designed for application from the air, and

Gordon Lindblom: a leader in fundamental studies on dispersant application systems

Others who have also played important roles are (in alphabetical order):

Ken Becker: co-developer of COREXIT 9500 and designer of the EXDET dispersant effectiveness test

Steve Bowes: industrial hygienist who provided human health guidance for dispersants

Hugh Brown (IOL): original investigator of dispersion tests in cold and icy waters in the 1990s

Brian Cashion: ExxonMobil's principal dispersant advocate/consultant in the 1980s

Andrie Chen: mechanical application specialist who co-developed the fire monitor concept for single point dispersant application

Jim Clark: ExxonMobil's lead toxicologist who advanced the concept of applying Net Environmental Benefit (NEBA) considerations for the use of dispersants in bays and near shore; advocate of the use of transient short-term toxicity testing; current leader of the dispersant R&D program

Greg DeMarco: dispersant advocate who represented Exxon in important 1990s UK field tests

Bob Fiocco: co-developer of COREXIT 9500; investigated the solvent's role in dispersant effectiveness; prime contact for SINTEF field dispersant studies in Norway during 1990s

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Anita George-Ares: toxicologist with over 10 years of fundamental toxicity studies on dispersants; drafted 2000 edition of the ExxonMobil Dispersant Guidelines; advocate of dispersants for fresh water

Ron Goodman: Imperial Oil's cold water expert; designed and ran cold water dispersion tests in an Alberta wave basin during the 1980s and 1990s

Bob Goodrich: dispersant advocate in 1980s; conducted fundamental cold water studies in 90s

Stu Horn: oil spill expert who had important roles in development of the ADDS PACK and in the API Seaspport near-shore experiments

Wolfgang Konkell: lead contact on all oil spill trajectory modeling activities across the company.

Dick Lessard: led the team that formulated COREXIT 9500; authored the 1994 edition of the Exxon Dispersant Guidelines; developed the ExxonMobil dispersant course; led the dispersant R&D effort 1990-2004.

Bill Lerch: ExxonMobil response manager who is a key advocate for broadening primary and secondary niches for dispersants as part of an overall spill response strategy

Bob Major: co-developer of fire monitor single point application of dispersants

Tim Nedwed: key investigator of means to extend dispersant effectiveness at long soak times and in cold climates

Jere Noerager: expert on dispersant application technology

Charlene Owens: Upstream dispersant specialist who coordinated fundamental studies of dispersant use in ice waters in early 2000s

Sal Pace: conducted size distribution experiments on dispersed oil droplets

Tom Parkerton: toxicologist who supported dispersant fate and effects studies

Max Robbins: microemulsion and oil colloid expert who conducted droplet size studies and holds 25 patents in the field, including on oil spill dispersants

Brian Steelman: early dispersant investigator who co-designed the Mackay-Nadeau-Steelman (MNS) effectiveness test

Tommy Tomblin: key advocate/developer of single point application techniques and dispersant stockpile manager and deployment strategist

Evan Thayer: industrial hygienist who provided human health guidance on chemical dispersants

Ramesh Varadaraj: scientist who conducted early fundamental work on the design and application of dispersants for heavy fuel oils

Marge Walsh: key participant in Exxon Chemical dispersant manufacturing for over 25 years

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1.0 PURPOSE OF THE MANUAL

This manual has been prepared to provide background and operational information on oil spill dispersants, how they work, and the incentives for their use, to personnel whose responsibilities include oil spill contingency planning and response. Based on over forty years of studies, chemical dispersants are considered an acceptable, and often preferred, means of minimizing the environmental impact of oil spills.

The principal ecological benefit of dispersant use is to keep oil from entering near-shore bays and estuaries, or stranding on shorelines, thereby protecting sensitive coastal habitats and the species that inhabit them. In every case where spill impacts have been studied, it is the species in the areas near or on shore that have been most affected by spilled oil (Lewis and Aurand, 1997). The main driving force for dispersants is to remove oil from the surface of water and prevent it from reaching these sensitive shoreline areas. When properly executed, waves and mixing energy distribute the oil as small droplets in the water column where it is diluted by currents and undergoes natural biodegradation. Although there are short-term, limited exposures of marine life to diluted oil, these exposures generally do not result in significant long-term ecological impact (NRC, 1989; Etkin, 1999).

A great deal of new information has become available on aquatic toxicity of dispersants, effectiveness in low-salinity water, application to heavy and weathered oils, and use in cold climates, since the 2000 edition of the ExxonMobil Dispersant Guidelines (this edition's immediate predecessor). World-wide regulatory approval of dispersant use has continued to expand and even consideration of dispersant application closer to shore has gained a level of acceptance in some locales. The U.S. National Research Council and the Coastal Response Research Center have defined remaining issues with respect to dispersant use and research to address these issues is underway. New information available on these and many other aspects of dispersant knowledge has been included in this volume.

This edition reflects significant change in presentation format versus earlier editions. The information has been assembled using the outline of the ExxonMobil Dispersant Course, which has been presented around the world with very positive feedback. The key authors of this revised manual are shown below. You are encouraged to contact any of them with feedback, comments, or relevant new data.

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2.0 EXXONMOBIL POSITION ON OIL SPILL RESPONSE

ExxonMobil's basic position on oil spill response is that no response option should be ruled out or constrained in advance. Ideally, removal of oil from the marine environment is preferred. However, past spill experience has demonstrated that a response composed only of mechanical recovery has distinct limitations due to low recovery rates, sensitivity to water currents, and effect of adverse weather conditions. To limit the environmental impacts of large oil spills, the response strategy must include all viable techniques, including preventive containment booming, mechanical recovery, dispersant application, and sometimes in-situ burning.

Chemical dispersion is an important option that should always be planned for early in the first stage of a response operation. It is a serious mistake to relegate dispersants to a fallback position to be considered only after mechanical response has proven inadequate. To do so risks losing the "window of opportunity" as dispersants work best in the earliest stages of response and delaying their use can waste valuable time and constrain subsequent response options if weather conditions deteriorate. Response decisions in the first stages of a spill response should be based on deployment of the most effective approaches to reduce the overall environmental impact. Given appropriate conditions, application of dispersants can rapidly reduce the impacts of an oil spill on the surrounding environment.

In considering how best to utilize dispersants, efforts should focus on applying dispersant on an oil slick before it approaches biologically-productive habitats such as mangroves, salt marshes, and estuaries. It is more beneficial for these habitats to be exposed to diluted oil in the water column than to concentrated floating oil that eventually strands and persists among them. A number of studies discussed in this manual have clearly shown that biological recovery from dispersed oil in the marine environment in open waters is much faster than that from untreated oil stranding in a sensitive, coastal habitat.

ExxonMobil believes that no minimum distance or depth limits should be placed on dispersant application in advance. In general, though, government agencies are reluctant to permit dispersant use close to shore or in water depths less than 10 meters. However, there have been occasions where some countries have safely applied dispersants directly on shorelines (Etkin, 1999). The key consideration should be the **net environmental benefit** of dispersant use in the overall context of the spill incident. For example, as discussed in this manual, studies on near-shore impacts of dispersed oil have shown that dispersion of oil into inter-tidal waters can substantially mitigate the overall environmental impact of spilled oil and accelerate the flushing of the oil from the area. These same tests also provided clear evidence that undispersed oil caused mortality of inter-tidal species and remained in the area for considerably longer periods. In light of this evidence, it is recommended that dispersant use should always be decided on a case-by-case basis regardless of the depth of the receiving water.

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Though ExxonMobil scientists formulated and developed the COREXIT line of dispersant products, the company is no longer commercially connected to the COREXIT line, which is now marketed and sold by Nalco Corporation. We are advocates of appropriate dispersant use, regardless of product type or source, since protection of the marine environment is the principal goal, and we remain optimistic that products with enhanced performance will continue to evolve. As improved lower cost products become available we anticipate being among the first to accept and use them, if and when needed.

3.0 GENERAL OVERVIEW OF OIL SPILLS AND RESPONSE OPTIONS

3.1 How Oil Properties Affect the Response Strategy

Once oil has been spilled, one of the most important response considerations is the type of oil involved. Each spill is unique and, depending on the type of oil involved, the preferred response can be quite varied. For example, extremely volatile oils that evaporate rapidly may require little or no intervention. In fact, containment of volatile products, such as gasoline, may be hazardous due to the potential accumulation of explosive vapors above the liquid, and is forbidden in some areas. At the other end of the spectrum, there are oils that are so heavy or have such a high pour point that they may be completely solid or submerged by the time response can be implemented. In between, there are innumerable types of oils representing a wide range of viscosities, pour points, densities, and volatile content. However, one aspect that is common for all persistent oil spills is that they require rapid response and prompt selection of appropriate countermeasures.

In addition to the wide range of oil properties, there are other challenges to developing effective response strategies, as listed in Table 3.1. Weather, climate, and time of year can all affect the ability to respond. Moreover, the changing nature of spilled oil over time due to weathering means that response strategies need to be continually assessed and adjusted during the course of a response, consistent with oil properties and behavior on any given day.

Table 3.1 Challenges to Oil Spill Response

Weather	<ul style="list-style-type: none"> • Containment and recovery may be ineffective in rough seas or high winds • On-water activities may be unsafe in very high seas • Weather (rain, fog) can limit dispersant application, depending on the aircraft and/or vessel being used
Seasonal Effects	<ul style="list-style-type: none"> • Short daylight times in arctic regions during winter • Ice cover seriously complicates response • High heat could limit work hours
Oil Weathering	<ul style="list-style-type: none"> • Oil properties constantly changing • Rate of change different for every oil and set of environmental conditions
Remote Locations	<ul style="list-style-type: none"> • No roads, airports or other infrastructure • No immediate logistical support
Wide Range Of Habitats	<ul style="list-style-type: none"> • Rocky shores to sensitive marshes • Response must be tailored to environmental sensitivity
Increasing Spill Area	<ul style="list-style-type: none"> • Slick continuously expands as oil spreads and thins • Response options become less efficient with time

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The added complications of a spill occurring in remote areas, perhaps with logistical support provided only by air or water, pose added difficulty during a response. Availability of heavy mechanical equipment that must be transported over roads for staging would be extremely limited under such conditions. Additionally, there is the need to consider the environmental sensitivity of the area into which the oil either was spilled or is moving toward. Strategic decisions must be made in full consideration of how delicate the environment is in order to prevent undue damage to the habitats by actions of the response itself. Finally, there is the challenge of the mobility of the oil as it constantly shifts under the influence of wind and current. The oil steadily spreads and thins thereby increasing the area over which response operations will be needed and reducing the amount of oil that can be treated or recovered from any fixed area of operation. Rapid response is the key to maximum efficiency and effectiveness of oil treatment and recovery.

3.2 Response Options

Unfortunately, no single strategy or response alternative is suitable for the entire range of oil types and conditions likely to be encountered. The selection of preferred countermeasures will vary with circumstances. If the oil is moving out to sea and is not a threat to any shoreline habitat or wildlife, it may be appropriate to take no action other than to **monitor and track** its movement. This may be especially true in the case when severe weather is either occurring or expected. While high energy seas can be very effective at dissipating the oil through natural dispersion, it must be remembered that a window of opportunity to treat or recover the oil may be lost if such an approach is taken. Slicks that were thought to be moving out to sea have, on occasion, changed direction and come ashore before other countermeasures could be implemented. With the passing of time, the effectiveness of all response options, including dispersants, will be diminished.

Before making the decision not to actively intervene with a spill, it is important to have a clear understanding of the prevailing winds and currents and the likelihood of oil stranding several days later. Use of oil trajectory models is essential for predicting the likely fate of the oil. One should also consider the offshore presence of migrating or spawning fish, marine birds, mammals, and turtles and the potential for adverse effects on these species if the oil is not dealt with.

Mechanical containment and recovery of the oil from the water has been the generally preferred oil spill control measure because it physically removes the oil from the marine environment. This is usually accomplished through use of devices such as containment booms and skimmers. The ExxonMobil Oil Spill Response Field Manual (ExxonMobil, 2005) provides excellent summaries of the design and capabilities of booms and skimmers. However, in many circumstances, physical removal is neither efficient nor practical. For example, experience has shown that mechanical response has poor recovery rates in open waters, and cannot adequately deal with very large spills, especially when the oil thickness has thinned to 1 mm or less. Picking up 10 per cent of the floating oil at a large spill is considered a success for mechanical recovery at sea (IPIECA, 1993). Mechanical response methods are most effective if the current is less than 1 knot and wave heights are less than 1-2 meters; most booms and skimmers are of limited use in

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moderate seas. Even in calm conditions, mechanical equipment alone cannot handle large spills if the oil has spread over large areas because the spill encounter rate is necessarily low. Storage of the recovered oil can quickly become a limitation as well. Finally, there is the practical challenge of conveying the equipment to the scene of the spill and deploying it. Since containment and recovery equipment is bulky, heavy, and requires substantial ancillary support equipment, such as forklifts, trailers, and cranes for staging and deployment, its use may not be feasible in remote areas with no logistical infrastructure. Offshore, the skimming boat has the required equipment but may be slow to arrive and may be limited by oil storage. *As a result, the most effective/efficient use of mechanical recovery strategies is on thick slicks in relatively calm water early in the response and close to the release point. Even so, such an approach can be limited by the possible presence of elevated concentrations of vapor and flammable gases.*

Burning of oil "in-situ" is another option for dealing with spills that has gained attention in the past 15 years, especially in North America. For in-situ burning to be effective on water, the oil thickness should be at least 2-3 mm. The key is to maintain the required thickness and sustain burning by pulling the oil against the current while it burns on the surface of the water inside a specially-designed fire-resistant boom. The oil must be relatively fresh and not contain too much water. Under ideal conditions, large amounts of oil can be removed from the water surface using this tool. During in-situ burns, however, much of the oil is converted to soot and smoke because of inefficient combustion, which can be problematic when a burn is conducted close to population centers. There is also a residue of 1-3% which can sink. The technique has obvious safety risks and only well-trained specialists should be involved in the planning and execution of this type of activity. Though pre-approved for use in parts of the U.S. and Canada, burning has not been extensively used on waterborne oil spills to date. Figure 3.1 is a photo of oil being burned in-situ at the *Exxon Valdez* spill in 1989. *In-situ burning is most applicable to slicks from continuous releases in calm waters, to restoration of oiled marsh areas, and to oil in icy waters.*

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Figure 3.1 In-Situ Burning of Oil on the *Exxon Valdez* Spill, 1989

Solidifiers are polymeric products developed over the past 30 years that react with oil and bind it in a cohesive mass, immobilizing it and reducing the rate of spreading and thinning. Solidifiers can also be used to control the rate of vapor generation from light oils and petroleum products, reducing explosion potential and human exposure. Most products are designed so that the solidified oil mass will float until fishnets, perforated shovels, or other pickup devices can physically remove it from the water. Solidifiers are usually applied as powders, granular mixes, or gels at high application rates, limiting their potential usefulness in responding to large spills at sea. *The preferred use of solidifiers is on small spills in bays and harbors or on land.*

Dispersants are used to break oil slicks into small, micron-sized droplets that then disperse to low concentration in the water column. Dispersants can be used over a wider range of slick thicknesses and sea conditions than the other response options discussed above. In fact, active seas are advantageous since they provide added energy to keep the dispersed oil distributed across the water body, offsetting the buoyant forces acting to re-surface dispersed oil drops. At small droplet sizes and low water column concentrations, the oil can be degraded by micro-organisms while exerting minimal harmful effects on nearby species. Dispersants have the unique advantage versus other options of being deployable by aircraft, making it feasible to treat large areas in a relatively short time period. A limitation to dispersant use is a time window of application that is typically limited to just a few days following a spill, making it imperative that

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application begin as soon as possible. *The preferred use of dispersants is on relatively fresh slicks in active seas.*

Table 3.2 summarizes the limitations and concerns of the available at-sea response options.

Table 3.2 Limitations and Concerns of Response Options

Monitor Only	<ul style="list-style-type: none"> • Winds and currents can change sending spill toward sensitive areas
Mechanical Containment and Recovery	<ul style="list-style-type: none"> • Limited to less than 1 knot current and 2 meter waves • Oil slick encounter rates are very low • Not efficient in thin slicks • Hampered by viscous products and debris • Requires storage for recovered oil and water
Burning	<ul style="list-style-type: none"> • Limited to low current and waves • Weathered oil can be difficult to ignite • Igniting emulsified oil is a problem • Requires igniters, heavy lift equipment, and special fire booms that are expensive • Fire boom has limited life • Must be sufficiently far away from populated areas
Solidifiers	<ul style="list-style-type: none"> • Not practical for open seas • Not effective on heavy or weathered oils • Requires collection of solidified oil
Dispersants	<ul style="list-style-type: none"> • Limited time window of opportunity • Viscosity and emulsification can reduce effectiveness

3.3 Strategy for Optimal Deployment of Response Equipment

Optimal response to a large spill will likely require a combination of response techniques using each in its most effective manner. Since a spill is rarely uniform in thickness, it is sensible to use the following guidelines in deploying the various response techniques.

- Deploy **mechanical equipment** in the thicker areas of darker oil, weather and sea state permitting, to maximize encounter rate. Take into account safety concerns associated with fresh spilled oil as this may limit where equipment can be placed. Avoid mechanical recovery efforts in areas that are silver- or rainbow-colored as the oil thickness in these lighter areas is probably 1 micron thick or less (< one thousandth of a millimeter), greatly reducing response efficiency.
- If **in-situ burning** is permitted, then it should be deployed in the thicker oil, again weather and sea state permitting. However, select an area so that there is no interference with any

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other operation and the distance from shore and the wind direction are such that the resulting smoke will not pose a concern to population centers or responders.

- Apply **dispersants** in conjunction with **mechanical recovery** and **burning** on the outlying untreated part of the slick that most threatens sensitive or important habitats and shoreline areas. Apply to dark oil, not to sheen or rainbow oil. Avoid spraying in areas where there are workers implementing any of the other options.
- If **mechanical recovery** and/or **burning** have been deployed and are nearing the limit of their effectiveness either due to weather changes or thinning of the oil, consider converting the entire response to **dispersant** application, provided that the oil properties are still suitable for dispersion.
- Use large fixed-wing aircraft to apply **dispersants** to broad uniform slick areas. Smaller aircraft, helicopters, and/or boats may be better suited for treating patches of oil or windrows because of their better targeting capability.

3.4 Widespread Support for Dispersant Consideration and Use

Dispersants provide an effective and practical first-line means to combat oil spills, along with other response options. Historically, though, they were viewed as a secondary or back-up response option to be only used in instances where containment and mechanical recovery were found to be insufficient for dealing with an oil spill. A good deal of the hesitation in using dispersants was due to uncertainty of their impact on the environment. However, much work has been done since the *Torrey Canyon* incident and current commercial dispersant formulations display lower toxicity than earlier products. Research in the last 20 years has shown that any concern should be focused on the effects of dispersed oil versus untreated oil, per the NEBA (Net Environmental Benefit Analysis) process, and not solely on the dispersant (NRC, 1989, 2005). As will be discussed later in the section on toxicity, the concentrations of dispersant normally encountered after application contribute minimally to a spill's toxicity.

In 1989, the U. S. National Research Council's (NRC) Committee on Effectiveness of Oil Spill Dispersants reported on an extensive assessment of the state of knowledge and practice regarding dispersant use. The Committee recommended that "*dispersants be considered as a potential first response option to oil spills, along with other response options*" (NRC, 1989). A follow-up NRC study published in 2005 re-affirmed the efficacy of dispersants as a first response option but further indicated that dispersants should be considered when mechanical response alone is clearly not sufficient (NRC, 2005, p. 280). The concern with this approach is how long it takes to clearly recognize that a mechanical response alone will not suffice. If a spill is 50 nautical miles offshore, mechanical equipment arrival and deployment alone can take up to 10 hours. Such a delay would waste valuable time for dispersant treatment, which can be implemented in as little as 3-4 hours, and could miss much of the window of opportunity for some oils.

If there is any doubt regarding the timeliness and effectiveness of response options, then dispersant use should be implemented immediately because, as the same 2005 NRC report states, "failure to make a timely decision regarding dispersant application is in actuality a decision not to

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use dispersants, and in some instances may place some natural resources at an increased and unnecessary risk” (NRC, 2005, p. 4). If a judgment of the adequacy of mechanical response cannot be confidently made at the beginning of a response action, then dispersants should be deployed along with mechanical and other options from the start. ASTM’s Standard Guide on Chemical Dispersant Use in Oil Spill Response states that each On-Scene Commander has available several means of control or cleanup for spilled oil. “Use of chemical dispersants should not be considered as a last resort after other methods have failed. Chemical dispersants should be given equal consideration with other spill countermeasures” (ASTM F 2205, 2004).

In 1993, at the request of the UK Minister of Agriculture, a review of procedures for testing and approval of oil spill dispersants was conducted as an outcome of the tanker *Braer* spill in the Shetlands in Scotland. MAFF (Ministry of Agriculture, Fisheries and Food), Warren Spring Lab, Marine Laboratory of SOAEFD (Scottish Office of Agriculture Environment, and Fisheries Department) and others participated in the review. The final report noted that the technique most frequently used in the UK for oil spill response *"is to deal with them at sea by applying oil dispersants from low-flying aircraft."* The report also stated that *"there is no evidence that properly stored and properly used modern dispersants are inefficient or are harmful to man or the environment"* (MAFF, 1994).

“Oil spill dispersants are a valuable tool for responding to marine oil spills. These chemicals can enhance the natural chemical and physical breakdown of oil and facilitate dilution and dispersion to the point that a spill causes less environmental damage — less shoreline oiling and less wildlife oiling.” (Etkin, 1999)

3.5 “Facts about Dispersants” (IMO/UNEP, 1995 p. 34)

1. “Most modern dispersants are relatively non-toxic and are less toxic than the oils they disperse.
2. Dispersing oil where there is sufficient water for dilution has never shown toxic effects on marine or benthic biota.
3. Toxic effects of using dispersant could be evidenced where there is little dilution potential, as in shallow bays or over shallow coral reefs.
4. Dispersants will generally remove a certain percentage or portion of oil from the sea surface if the particular dispersant is “compatible” or effective with the oil type/composition, etc.
5. The percentage of oil removed depends on oil and dispersant composition and on sea energy.
6. Many oils will disperse naturally in higher seas. Dispersants serve to enhance this process.
7. Heavier oils generally disperse poorly. This is oil composition-dependent.
8. Due to weathering processes, the time window for effective dispersion can be short, often one to two days.

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9. Dispersants function by assisting oil break-up into small droplets which behave as if neutrally buoyant in the water column.
10. Dispersant effectiveness is also dependent on proper application. This is achieved by applying an optimal droplet size on the thicker portion of the oil slick.”

“Consider some of the worst and most distressing effects of major oil spills: dying wildlife covered with oil; smothered shellfish beds on the shore; mangrove swamps full of oil and dying trees. Any method of response that can help to minimize this destruction is worthy of consideration. Dispersants are such an option. By breaking up slicks they can lessen those effects associated with oil coating and smothering. There is clear scientific evidence that in some cases they can reduce biological damage” (Jenifer Baker, in IPIECA, 2001).

“The few studies undertaken in areas where dispersants have been used extensively have not demonstrated significant effects on populations of particular species or biological communities. Conclusive evidence of increased tainting of commercial species resulting from dispersant usage is also not available.” “In areas where the dilution potential is great, such as the open sea, elevated concentrations are unlikely to persist for more than a few hours and significant biological effects are therefore improbable.” Despite greater risk, “the careful application of dispersants (in shallow water close to shore) may on these occasions be beneficial overall, if damage to adjacent ecologically sensitive shorelines is reduced as a result” (ITOPF, 1987).

In summary, there is broad consensus that dispersants should be an integral part of oil spill contingency planning and response and should always be considered with other techniques as a first response option. Because of advances made in formulation, early concerns regarding the potential adverse effects of dispersants have diminished significantly. The next section discusses the role of Net Environmental Benefit Analysis (NEBA) in deciding how best to deploy dispersants.

4.0 NET ENVIRONMENTAL BENEFIT ANALYSIS (NEBA) CONSIDERATIONS

4.1 All Response Options Have Advantages and Disadvantages

Once oil has been spilled, it is important for the decision makers to realize that regardless of what action is taken, there will inevitably be some impact. With this in mind, the concept of Net Environmental Benefit Analysis, or **NEBA**, was developed in the early 1990s by NOAA (NOAA, 1990) and Dr. Jenifer Baker of the UK (Baker, 1995) so that the cleanup decisions that are made keep the adverse environmental and socioeconomic impacts to a minimum. It is, in essence, the selection of actions that lead to the lowest overall negative impact. Following NEBA in order to arrive at the specific strategy that is best for the local environment, responders will:

- Weigh the relative importance of all resources. This involves collecting information on physical characteristics, ecology, and human use of all resources in the area of interest. Hopefully, these have been defined to reflect local interests in earlier contingency planning and are available for review and consideration.
- Refer to the local and regional priorities. In some areas, tourist amenities may sometimes take priority over natural resources.
- Get all parties to understand that, regardless of the course taken, some impact is likely to result. This can be challenging because local stakeholders may demand that actions be taken that will result in no impact, a scenario that is generally not possible.
- Weigh the advantages and disadvantages of all response options in light of local priorities and the many differing points of view and decide the best course with buy-in from all key stakeholders. This should be done promptly to mitigate delays caused by objections and possible confrontations.

The International Petroleum Industry Environmental Conservation Association (IPIECA) has defined a priority ranking (authored by Jenifer Baker and Tim Lunel) to be used to make decisions in the face of conflicts of interest (IPIECA, 2000, Volume 10). The key points from IPIECA are:

- Wildlife (e.g., seabirds, and turtles) typically merits higher priority than shore organisms (e.g., seaweeds, barnacles, and marsh grass) because recovery or replacement of wildlife populations is likely to be comparatively slow and difficult.
- Fish and shellfish resources merit higher priority than amenity sand beaches, jetties, and slipways as oily taint may take months to clear from fish, whereas surfaces of concrete or firm sand can be cleaned and restored to usefulness relatively quickly.
- Wildlife species may sometimes merit a higher priority than fisheries, notably in cases where dispersant treatment reduces the threat to seabirds at the expense of increasing the tainting of fish. The relative priorities of these species will vary with location and should be decided in advance during pre-planning activities.
- The viability of most fish populations is less threatened by tainting than seabird populations are threatened by surface slicks.

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In applying NEBA to the selection of a dispersant strategy, the question that needs to be answered is: **Does dispersing the oil into the water column offer more benefit (i.e., cause less harm) than leaving it on the surface if it cannot be adequately removed by mechanical means?**

Some example dilemmas that responders could face in balancing advantages and disadvantages as part of a NEBA include:

- Dispersing the oil into the water column could impact marine life such as fish and plankton, but leaving it on the surface could kill seabirds, turtles and other wildlife that live near or on the ocean surface (see Figure 4.1), or it could end up on amenity beaches, severely impacting the local tourist economy (Figure 4.2).
- Dispersing oil into the water could harm valuable coral reefs, but if left on the surface the oil could enter a mangrove forest with devastating effects on sensitive mangrove trees. Mangroves and coral are often found along the same shorelines.
- Dispersing oil into the water column could have serious detrimental effects on sea grasses, kelp and other marine vegetation, but if the oil comes ashore into a sensitive marsh area, it could destroy trees and grasses that underpin the integrity of the shoreline and lead to destruction of important nursery areas (Figure 4.3).



Figure 4.1 Wildlife Resources at Risk From Spilled Oil

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These are hard choices and reaching consensus on the best course of action can be extremely difficult during an oil spill emergency. Some of the various stakeholders (e.g., fishermen, park officials, natives who live off indigenous resources, etc.) could be unduly guided by their own vested interests in establishing their positions about response priorities. Such difficult issues are clearly best decided well in advance of any spill emergency when all the issues and local priorities can be balanced and discussed in-depth and without the undue pressure of a crisis situation. That is the purpose of contingency planning.



Figure 4.2 Lebanese Coast Following September 2006 Bombing Attack on Jiyéh Power Plant (CEPRECO, 2006)

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Figure 4.3 Oiled Trees and Vegetation (IPIECA/TOPF, 2007)

In the case of dispersants, the aim of contingency planning is to designate areas that are clearly suitable for pre-approved dispersant use as well as the conditions under which they will be permitted, based on thorough consideration of all local resources and priorities. During the planning phase, all important resources can be identified and relative priorities assigned and agreed to because there is ample time to consider all sides of the issues and build consensus on the best overall NEBA course that should be taken in the event of a spill. That allows the local incident commander to quickly make final decisions during an incident that fully reflect the broad range of priorities representative of the entire community.

4.2 When Dispersants Are a Clear NEBA Preference

In their 1997 paper, “Putting Dispersants to Work: Overcoming Obstacles,” Lewis and Aurand conclude that “Spills which have had obvious and significant biological impacts have always involved near-shore or inter-tidal accumulations of oil” (Lewis and Aurand, 1997). They further assert: “The available evidence suggests that in situations where sensitive shoreline or near-shore habitats are threatened, there can usually be a net environmental benefit to dispersant application if the oil cannot be prevented from entering the area by other means.” In other words, **under a NEBA analysis, dispersant use offshore is preferred to deployment of mechanical response equipment alone, if the mechanical response unaided might allow oil to enter shoreline habitats.**

ExxonMobil is aware of the impact oil can have on shoreline when it comes ashore as a result of not applying dispersants. In 1989, the *Exxon Valdez* tanker went aground on Bligh Reef in Prince William Sound (PWS), Alaska, spilling nearly 11 million gallons (41,000 metric tonnes).

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Dispersants had been pre-approved for certain parts of PWS but the permit conditions included a provision for testing for efficacy before obtaining approval for widespread use. By the time testing had been completed and approval granted, a fierce spring storm arose that distributed the oil over much of PWS and the Gulf of Alaska, impacting some 2000 km (1300 miles) of shoreline, much of it sensitive. The resulting damage was extensive. The cost of cleanup and remediation totaled billions of dollars.

Many people still believe the *Valdez* was the largest spill of all time. However, while the spill is the largest in U.S. history, it was relatively low magnitude, ranking number 57th when compared on the all-time list (Cutter Information, 2000). For reference, the 1991 Persian Gulf spill during the First Gulf War, had a volume of over 240 million gallons (909,000 tonnes). Although it was relatively modest on a worldwide scale, the *Valdez* spill gained its notoriety because of the locale in which it occurred and its extensive shoreline impact. Some have expressed the view that oil dispersant use at the *Valdez* spill would have significantly reduced the impacts and should have been applied at first chance (Davidson, 1990, quoting Dr. James Butler; Clayton McAuliffe, 1991).

4.3 Eco-System Recovery Time is an Important NEBA Consideration

As previously noted in the IPIECA Guidelines, one of the important factors to consider in doing the Net Environmental Benefit Analysis in connection with dispersant use is the relative recovery time for each of the species that might be impacted by oil, whether dispersed or not. Many bird species, for example, produce only one or two chicks per year so replacement could take considerable time if a significant fraction of a particular population is impacted. Also, some oil-sensitive vegetation, such as mangroves, can take several decades to reach a level of maturity at which they can function as a vital component of the eco-system. In making decisions that could affect the survival of such sensitive species, the relative recovery time can be a key consideration.

In 1993-94, noted scientists and professors from across England and Scotland, under the auspices of Aberdeen University Research and Industrial Services Ltd. (AURIS), conducted an extensive review of available worldwide literature on the effects of oil spills and found that ecological recovery of impacted shore biota usually follows natural time scales of up to three years for rocky shores and up to five years for salt marshes, regardless of cleanup (Sell et al., 1995). Recovery is defined for this purpose as the time it takes for a habitat to restore the diversity and abundance to the pre-spill range. In a subsequent follow-on study, AURIS investigators extended the review to more sensitive resources, including tidal flats, sea grasses, coral reefs and mangroves. Here the recovery times following impact were measured in decades—up to 80 years to fully replace a healthy mangrove forest (AURIS, 1995). Table 4.1 summarizes the habitat recovery data.

Table 4.1 Biological Recovery Times for Oil-Impacted Shorelines (AURIS, 1995)

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Habitat	Recovery Time
Rocky Shores	0.5 – 3 Years
Marshes	2 – 5 Years
Tidal Flats	5 – 10 Years
Coral Reefs	10 – 50 Years
Mangroves	25 – 80 Years

On the other hand, the regeneration time of most marine species is quite fast. For example, zooplankton, the water column community most likely to be impacted by the dispersion of oil, is abundant and constantly re-colonizing. Recovery of zooplankton would not be measured in years or decades but in weeks to months. Similarly, algae comprising the phytoplankton are ever present and can replace themselves in a day or less. Shellfish may take somewhat longer but their recovery is accelerated by the vast volume of eggs produced by just one individual—millions of eggs from a single bi-valve, for example. Major impacts to adult fish populations from dispersed oil have seldom been recorded, except when fish were confined in farms, as at the *Braer* spill. Fish have an innate ability to detect the presence of oil and will rapidly swim away from impacted zones. Comparing these recovery considerations for marine species with the ability of birds to lay only a few eggs over a year or to a mangrove reaching maturity in decades makes it clear why recovery time is an important consideration in setting response priorities.

In summary, Net Environmental Benefit Assessment favors the use of dispersants in offshore waters; the alternative is that oil might reach sensitive habitats or impact clusters of wildlife, such as birds, which generally have longer recovery times.

4.4 Additional Supporting Endorsements:

- **US National Research Council:** *The overall ecological impact of oil will likely be reduced by dispersion (NRC, 1989).*
- **IPIECA:** *The advantages and disadvantages need to be considered with reference to local conditions during the contingency planning process. Decision making is not a purely scientific process; it involves balancing a variety of interests. In most regions it is likely that the dispersant option could offer a net environmental benefit for some spill scenarios (IPIECA, 1993).*
- **IMO/UNEP:** *The possible detrimental effects of the use of dispersants might be offset by the gains that result from keeping other parts of the environment clear of oil (IMO, 1995).*
- **ITOPF:** *On occasions the potential benefit gained by using dispersants to protect coastal amenities, sea birds and intertidal marine life, may far outweigh any potential disadvantages, such as the temporary tainting of commercial shellfish. Conversely, the dispersant option may be rejected in fish spawning areas in the open sea even if the risk of damage is very low and would not normally be advised close to industrial water intakes,*

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shellfish beds, coral reefs or within wetland regions. Despite the difficulties, it is important that an order of priority for the resources to be protected is established and the circumstances under which dispersants may be used are agreed upon before the occurrence of a spill (ITOPF, 1987).

- **Dr. Jenifer Baker:** *The overall conclusion was that the impact of the spill on the ecology and environment of south Shetland has been minimal (Baker, 1995).* These were Dr. Baker's comments on the impact of the *Braer* tanker spill in the context of findings relevant to NEBA of dispersant use. Much of the cargo of the *Braer* was dispersed into the near-shore waters of the Shetlands with minimal impact. This is one of the few major dispersed oil spills whose marine impacts have been subsequently monitored in detail over a period of several years.

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5.0 DISPERSANT CHEMISTRY AND MECHANISM

5.1 Makeup of Dispersants

Dispersants were first applied to oil spills in the 1960s. They are formulated as liquids containing one or more surface active agents (surfactants) and one or more solvents. Surfactants have chemical structures that enable them to facilitate the movement of hydrocarbons into water by reducing the interfacial tension between the oil and the water. They were originally developed for use in detergents, shampoos, cleaners, and dish soaps to help water extract and remove oily matter from hair, carpets, dishes, etc. Some are used in the food industry. They do not dissolve oil, but rather distribute it in the water as extremely small suspended droplets. They are effective because they are formulated to have two functionalities built into a single molecule. One end of the molecule is lipophilic, literally meaning “oil-loving” and the other end is hydrophilic or “water-loving.” With its two different ends, the dispersant molecule acts as a connecting “bridge” between the oil phase and the water phase. Surfactants used in today’s dispersants are of relatively low toxicity and are especially selected for application to the marine environment

Solvents are used as carriers for the surfactants, which are either solid or very viscous liquids. Solvent is also necessary to reduce the viscosity of the final dispersant mix so that it can be pumped and properly applied by spray equipment. In addition, the solvent facilitates penetration and mixing of the surfactants into the oil slick, particularly for heavy and weathered oils. The solvent can also help achieve the proper concentration of surfactants for optimum application.

The three main classes of solvents used in dispersant formulations are water, hydrocarbon, and hydroxy compounds, such as glycol ethers and alcohols. Aqueous solvents permit the surfactant(s) to be educted into a water stream as a convenient method of application onto a spill. Hydrocarbon solvents enhance mixing into spilled oil. Hydroxy compounds can mimic the functions of both aqueous and hydrocarbon solvents.

Compositions of the various commercial dispersant products vary widely. Not only do the specific surfactants and solvents differ in molecular structure but the percentage of surfactant in the product also differs markedly. Some dispersants may contain as little as 10 to 20% surfactant, while others contain over 50%. This latter group is sometimes referred to as "concentrates." The variation in surfactant content partly accounts for a wide range of observed dispersant effectiveness and their market prices. Generally speaking, the higher the surfactant content, the more effective the product is at a given application rate.

5.2 How Dispersants Work

Figure 5-1 illustrates the overall dispersion mechanism comprising the key steps:

- 1) The dispersant is applied to the oil slick at the proper dosage.
- 2) The dispersant mixes into the oil and the surfactants diffuse to the oil-water interface.

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- 3) The surfactant molecules orient themselves at the oil-water interface and reduce the oil-water interfacial tension, a reflection of the basic molecular incompatibility of the two liquids.
- 4) The oil slick readily breaks up and disperses into fine droplets, facilitated by water movement/agitation.
- 5) The solvent partitions itself in the water and oil, the relative degree depending on its nature. For example, aqueous solvent would mostly migrate to the water phase. Hydrocarbon solvent would remain in the oil.

Dispersants are applied either neat or suspended in a water stream as tiny droplets onto the surface of the oil (Figure 5.1 1). The inclusion of a solvent helps move the surfactant into the oil layer. Because surfactant molecules contain both water-compatible and oil-compatible groups, the surfactant is not completely at ease in either the water or the oil phase and will thus align itself at the interface between the phases (Figure 5.1 3). This ability to reside at the interface is the basic reason that the materials are described as surface-active agents. The orientation of the surfactant at the interface reduces the interfacial tension that separates the two phases and enables an oil slick to break up into finely dispersed oil droplets. Some energy is needed to promote movement and dispersion of the small oil droplets into the water column but this energy can be supplied either by the natural wave motion and currents of the sea or by mechanical means such as induced turbulence from the propellers of work boats. The greater the available energy, the more quickly the oil will disperse and the finer the dispersed oil droplets will be.

As the oil enters the water phase as very small droplets (1-30 microns for a potent dispersant), surfactant molecules envelop the oil droplets with water-compatible ends facing out, rendering them stable in the water (Figure 5.1 4). The surfactant coating effectively prevents the re-coalescence of the droplets, allowing them to remain at their initial size until they are sufficiently far apart that collisions leading to coalescence are improbable. The presence of the surfactant offsets the normal rejection of the oil by the water and, because the hydrophilic ends have some polar-bonding attraction to the water molecules, the oil droplets tend to be less buoyant and more resistant to rising to the surface than without surfactant. As a result, Stokes' Law does not rigorously apply to dispersed oil droplets as long as the surfactant remains in place around the oil drops. The tiny drops will be carried by the water currents and distributed primarily into the top 10 meters of the water column. The net buoyant forces that remain keep the drops from sinking much lower.

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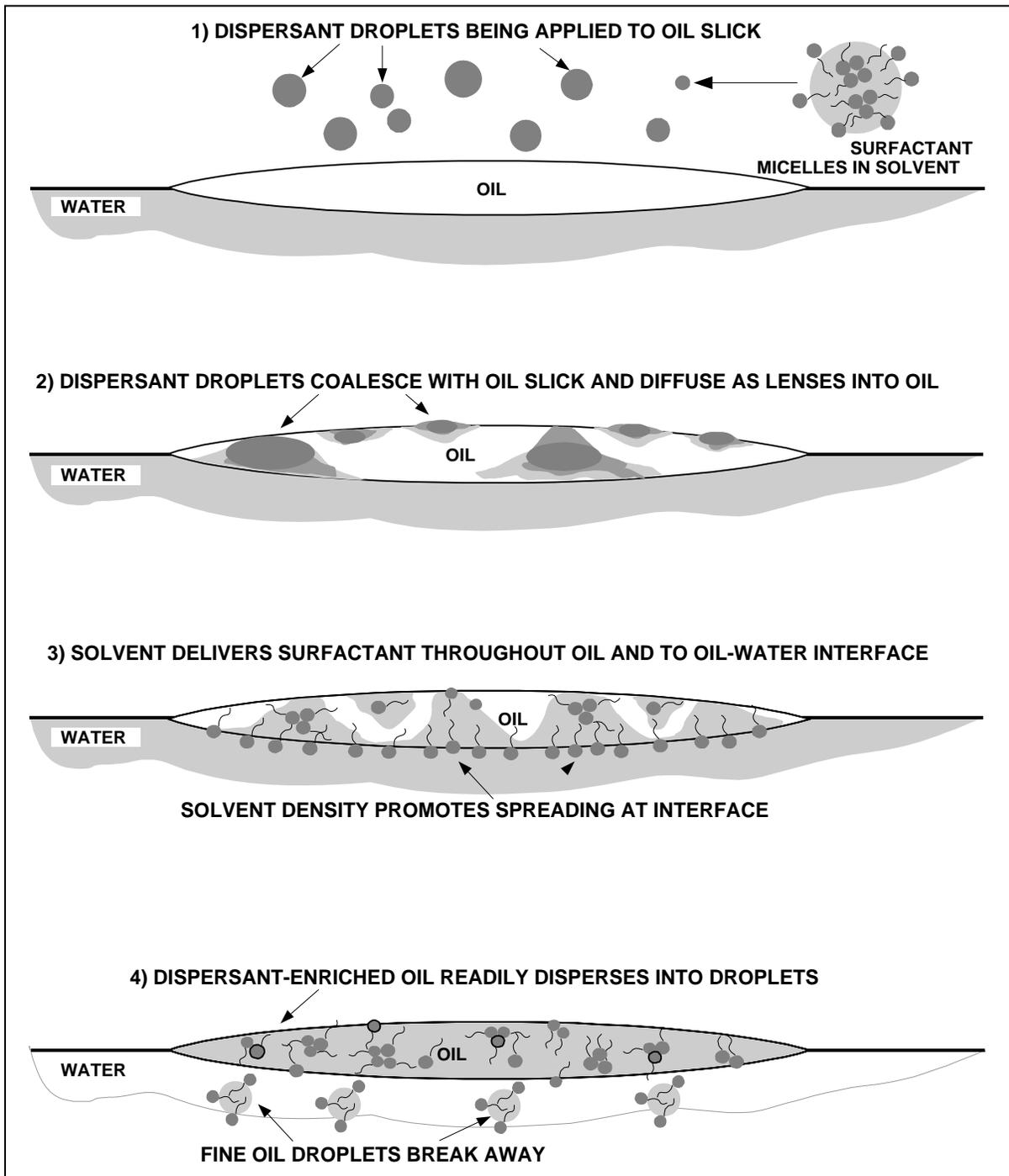


Figure 5.1 Mechanism of Chemical Dispersion

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5.3 The Goal

The objectives of dispersion are to remove the oil from the surface, where it is at its most potentially toxic concentration and its environmental fate is uncertain; dilute it into the water column to low concentrations before it can significantly impact biota; and facilitate its ultimate biodegradation. This is the importance of mixing energy, as it directly affects the rate at which this formation of small oil droplets and subsequent dilution occurs. Some of the more effective dispersant concentrates reduce interfacial tension to such a low level that very little energy is required for oil film breakup, even at low treat levels, i.e., low dispersant-to-oil ratios (DOR).

As will be discussed in a later section, measurements made following test and actual field dispersions indicate that dispersed oil levels are usually well below 100 ppm immediately after dispersing an average oil slick of 0.1-0.3 mm, dropping to less than 1 ppm in a matter of hours. That means that, by using chemical dispersants, oil concentrations can be very quickly reduced from whole oil at 1,000,000 ppm on the surface to less than 100 ppm in the water column. That represents a reduction in concentration by a factor of over 10,000 in a very short time. In a matter of a few hours, a one million-fold reduction in concentration may be obtained. Because toxicity is directly related to concentration and the duration of exposure, the benefit in reduced toxicity that results from applying dispersants and diluting oil in the water column is significant and obvious.

6.0 ADVANTAGES AND DISADVANTAGES OF A DISPERSANT RESPONSE

6.1 Advantages

The most important advantage of a dispersant response is that **it removes oil from the surface of the water** thereby lessening the probability of oil impacting shorelines, sensitive habitats, and wildlife found on or near the sea surface. By putting the oil into the water column, it is no longer subject to the forces of the wind, which could blow it toward shore, but instead is propelled by currents which are far less likely to move directly into shore. Other key advantages of dispersant use are:

- **Dispersants can be used over a wider range of environmental/meteorological/oceanographic conditions than other options.** For example, they can be more effectively applied in harsher weather (e.g., rough seas, strong winds up to 35 knots, and high waves over 6 feet) and on lower oil thickness (less than 1 mm) than other options. Dispersant effectiveness is enhanced by higher sea energy. The weather “Window of Opportunity” is much wider for dispersants than for mechanical recovery and burning, which are for the most part limited to low currents and reduced wave heights.
- **Dispersants can be applied to cover much greater spill areas in a given time than other response options.** Dispersants can be applied by fixed wing aircraft and helicopters at application speeds of 80-150 knots and by workboats at application speeds of 5-10 knots. This means improved response time and more rapid treatment of large spills. Table 6.1 (from Allen, 1988) compares instantaneous areal coverage rates for various treatment platforms, not considering lost time due to transit, turns, repositioning, re-load, down-time, etc.

Table 6.1 Areal Coverage of Response Platforms (Allen, 1988)

Platform	<u>Acres/Hour</u>	<u>Hectares/Hour</u>
Mechanical		
• Small Skimmers	0.2 – 2.6	0.1 – 1.1
• Medium Skimmers	3.5 – 14	1.4 – 5.6
• Large Skimmers	21 – 70	8.5 – 28
Burning	5 – 31	2 – 12.7
Dispersants		
• Vessels	28 – 140	11 – 56
• Small Planes/ Helicopters	193 – 893	90 – 360
• Large Aircraft	1750 – 5000	700 – 1980

- **Dispersants slow down the emulsification process (mousse formation).** If dispersants are under-dosed and do not immediately disperse the oil, they still act to neutralize the chemical and physical forces that create water-in-oil emulsions. Slowing the formation of

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emulsions keeps the oil amenable to dispersion for a longer period. Even if emulsions have already formed, the surfactants in dispersants can break these emulsions making the oil more suitable for either dispersion or mechanical recovery.

- **Dispersants accelerate the biodegradation of oil.** Biodegradation is the breakdown of organic matter through the use of microorganisms. Much of the broken down matter is eventually converted to carbon dioxide and water. Biodegradation requires organisms, water, oxygen, and nutrients such as nitrogen and phosphorus, all of which are abundant in the ocean. It is a multi-phase rate process, which means that it is driven by the concentration gradient and contact surface area. In the case of oil droplets, the smaller the droplet size, the greater the contact surface area per unit weight and therefore the faster the rate of degradation. Dispersants accelerate biodegradation of oil versus, say, physical dispersion of oil, because they produce much smaller droplets—typically in the range of 1-30 microns diameter (Robbins, et al., 1995)—and they enhance the bacterial colonization rate of dispersed oil droplets. Oil present in 20 micron (.02 mm) diameter droplets has a surface area 10 times that of the same quantity of oil present in 200 micron (.2 mm) droplets. In the 1960s, ZoBell reported biodegradation rates one to two orders of magnitude higher in laboratory experiments in which oil was emulsified (ZoBell, 1963).
- **Dispersants make oil less adhesive**, reducing the tendency to stick to sediment, sand, wildlife, vegetation, rocks, and other solid surfaces (Wilson and Putnam, 1982). Oil is hydrophobic and attaches to a foreign surface mainly as a means of separating itself from the chemically-unfriendly water structure. Dispersed oil droplets, on the other hand, are more compatible with water because of the surfactant layer that envelops them. The outer ends of the surfactant molecules are predominantly hydrophilic, resulting in oil droplets that are accommodated in the water phase and are less prone to attach to solid surfaces.
- **Dispersants offer a significant cost benefit.** Etkin summarized the cost comparison for spills on which dispersants were used versus spills on which they were not, based on data from the Oil Spill Intelligence Report International Database. The data show an 80% lower response cost when dispersants are used (Etkin, 1999). Presumably this reflects lower shoreline cleaning and disposal costs for oiled debris, response material and recovered oil. It does not include the cost of maintaining stockpiled or stand-by equipment. Table 6-2 summarizes the key data:

Table 6.2 Oil Spill Cleanup Cost Comparison in 1999\$ (Etkin, 1999)

Technique	Mean Cost/Gallon	Mean Cost/Tonne
Dispersants Only	\$7.27	\$2,137
Dispersants Primary Method	\$8.51	\$2,502
Dispersants Secondary/Tertiary	\$47.37	\$13,927
No Dispersants, Other Methods	\$42.61	\$12,527

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- **Dispersants minimize the generation of oily waste.** Dispersants do this by using the force of nature in the sea to degrade the oil through biodegradation. If dispersants are used properly and disperse the majority of the oil, the volume of waste oil and contaminated materials that needs to be disposed of via costly disposal options will be significantly less than for conventional mechanical response routes. This benefit also applies to an effective in-situ burn, though burning does result in a small amount (less than 5%) of residue to be disposed.
- **Chemical dispersants help prevent re-coalescence of small oil droplets once they are formed.** Unlike physical dispersion, the applied surfactants remain at the oil-water interface of the chemically dispersed oil droplets long enough to act as a barrier between droplets, which may otherwise randomly collide with one another and coalesce, until they are sufficiently far apart (NRC, 1989; API, 1999).

6.2 Disadvantages

The key disadvantage of dispersant use is that **oil is transferred into the water column** and could adversely affect some marine organisms that might not otherwise be impacted by oil (IMO/UNEP, 1995). Other disadvantages include:

- **Dispersants in oil may reduce the performance of other response methods**, notably that of oleophilic skimmers. If dispersants are applied and do not completely disperse the oil, the effect of residual surfactants on oil adhesion previously mentioned under “Advantages” may reduce the efficiency of skimmers whose recovery principle is based on oil adherence. Reduced performance is not a specific concern for other types of skimming devices such as weir skimmers, paddle belt skimmers, vacuums, etc.
- **Dispersants are not universally effective on all types of oils.** For example, some dispersants use weak solvents, including water, and have low surfactant content. These are best used on lighter oils and may not be as effective on more persistent or weathered oils. Some dispersants are formulated specifically for heavy and weathered oils but even these lose effectiveness as the oils become too viscous or solidify because of high pour point. In addition, dispersants may not be 100% effective in cases where they are improperly applied.
- **Dispersants may increase the penetration of oil into loosely compacted sediments and burrow holes** that would not have had oil intrusion otherwise (IMO, 1995). If used on or close to shore, dispersants make the oil more mobile in sub-surface habitats and could result in this effect.
- **Dispersants add to overall contaminants** by contributing another 1-5% of additional chemical material to the oil already spilled.
- **Dispersants lose effectiveness with time** because of weathering of the oil so there is a limited time window for effective application. It is critical that dispersant contingency plans include provisions for rapidly delivering dispersants on-site and ensuring continued application within the first 1-2 days. This issue becomes less critical in the case of an ongoing release.

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- **Many commercially available dispersants** are formulated for use in sea water and **do not work in fresh water**. However, there are some products that work in fresh water. Caution is needed in the selection of products for lakes and rivers.
- **Most dispersants require some minimum level of energy** to be effective in generating small dispersed oil droplets. Application in very calm seas may be ineffective if the forecast does not anticipate active seas developing 24-48 hours following application. Such a scenario would favor mechanical response.
- **Dispersant application by air requires large stand-by aircraft and supporting systems and staff in constant readiness.** Costs for this are best borne by multiple partners through cooperative agreements.
- **Use of dispersants on patchy slicks, such as windrows, can be inefficient and wasteful,** depending on the application equipment platform's ability to target.
- **Dispersants must be registered and approved in advance,** unlike mechanical response options.

6.3 When to Use Dispersants

Unless it is absolutely clear at the start that a spill can be completely contained and recovered, dispersants should always be considered as a strategic response tool, as long as they have been provided for and vetted in contingency plans and the resources are in place to implement a rapid (1-2 days) deployment. Conditions under which dispersants should be considered are given below:

- When sea and weather conditions preclude the use of any mechanical recovery or burning options. However, severe fog, lightning and precipitation could also limit dispersant activity. It is important to emphasize that many oils disperse naturally, without benefit of any chemical. In extremely rough seas (Table 15.7), dispersants may not be required at all.
- When natural dispersion is not sufficiently rapid.
- When oil is moving toward sensitive shoreline and all possible measures of control are called for to minimize impact based on NEBA.
- When birds are abundant in a spill area (e.g., during migration season) and there is potential for extensive contact with the surface oil before it can be recovered.

6.4 When Not to Use Dispersants

There are some situations that warrant careful evaluation before undertaking dispersant application. They are listed here as scenarios when dispersants may not be appropriate. However, they should always be considered in light of what sensitive resources might be at risk if dispersants are not used and whether or not these other resources are of higher priority than any marine life that might be threatened by dispersion. With that proviso, dispersants should generally not be used:

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- In shallow water (less than 10 feet) with poor circulation, such as protected bays and harbors. Use of dispersants in confined waters with low dilution could have higher toxic impact from oil than in open water where oil concentration can be quickly reduced.
- Near intakes for desalination or potable drinking water plants that cannot be closed while the dispersed oil plume is in the area of the intake.
- In the vicinity of aquarium intakes.
- Over active fish spawning areas, either wild or fish farms.
- Directly over shallow coral reefs. Dispersants can be applied once the oil has drifted away from coral or it may be preferable to allow the oil to strand on low productivity sandy beaches and implement cleanup of the sand. The socio-economic impacts of oiled beaches on tourism would need to be considered as part of the NEBA.
- Over mariculture and other sources of indigenous food grown in the marine environment.
- On oil that has solidified or reached extremely high (>20,000 cSt) viscosity.

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7.0 DISPERSANT EFFECTIVENESS

7.1 Factors Affecting Effectiveness

The factors that affect dispersant effectiveness can be grouped into two categories: the oil's properties and the environmental conditions. The influencing oil properties are:

- **Viscosity.** As oil weathers, it loses lighter ends leaving behind the larger, more bulky molecules that affect the oil's viscosity, or ability to flow. At viscosities of 1000-2000 centiPoise (cP) or less, most oils should be readily dispersible (IPIECA, 2001). A cP is the metric viscosity equivalent of the SI system's milliPascal second (mPa.s). As the viscosity rises above 2000 cP, some of the weaker dispersants will lose their capability; however, some of the more robust formulations will be effective even up to 10,000 cP. Only the most powerful products will work above 10,000 cP. At viscosities above 20,000 cP, it is likely that dispersants will not exhibit high rates of effectiveness, but a confirming test could be of value since viscosity is only a gross indicator of an oil's composition and some oils above 20,000 cP may still be dispersible and offer Net Environmental Benefit.
- **API Gravity.** This is a scale based on the inverse of specific gravity i.e., the lower the specific gravity, the higher the API gravity. The definition of API gravity is:

$$\text{API Gravity} = (141.5/\text{Specific Gravity @60}^\circ\text{F}) - 131.5$$

A very low specific gravity (density) material like gasoline has an API gravity of 62 whereas a heavy crude with about the same specific gravity as water (1.0) would have an API gravity of 10 (API, 1999b). As a rule of thumb (John Yeager and Associates, 1985), oils with API gravity above 45 (0.80 g/ml) do not need to be treated with dispersants because the oil is non-persistent and will evaporate and/or dissipate quickly. Oils with API gravities between 17 and 45 are generally dispersible by a wide array of dispersant products. Heavy fuel oils with API gravity below 17 (0.95 g/ml) may be dispersible but only by the most robust products and at higher Dispersant to Oil Ratios (DORs) than would be applied to disperse higher API gravity products.

- **Pour Point.** The pour point is the temperature, or range of temperatures, at which oil begins to pour as the temperature rises. Conversely, it is also the temperature at which oil begins to solidify as temperature is reduced. Each crude oil has its own pour point reflecting its unique blend of hydrocarbon molecules. Most oils solidify at temperatures well below the freezing point of water. Some oils (a few percent), however, have high wax content and solidify at relatively higher temperature, some higher than ambient water temperatures even in temperate and tropical regions. Once this occurs, the oil will be solid and resist dispersion and a dispersant response should be carried out only after pre-testing confirms the oil is dispersible.
- **Emulsion-Forming Tendency.** Emulsification is the incorporation of seawater droplets into the oil matrix in a fairly stable manner, and occurs especially when sea energy is high. The prevailing thinking is that oils can interact with water to varying degrees, depending on the amount of stabilizing molecules, such as asphaltenes, resins and porphorins, present in the crude. Some oils have very low amounts of these materials and do not form emulsions at all. As oil weathers, the concentration of asphaltenes increases

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until reaching a critical level at which their precipitation may occur and cause emulsification. The asphaltenes impart a holding force between the small water droplets and the oil that makes the mix extremely stable (Fingas, et al, 2001). Fresh oil can also emulsify under the action of metal porphyrins and the cumulative amount of nickel and vanadium metals has been used to gauge emulsification tendency of fresh oil (Canevari and Fiocco, 1997). Oil emulsions can reach water concentrations exceeding 80%, turning the oil into a near-solid brownish material, often referred to as “chocolate mousse,” dramatically increasing the total volume of contaminated material to be handled.

The ability of dispersants to “break” these emulsions prior to dispersion will depend on the types of surfactants in the dispersant (some surfactants have more demulsifying strength than others) and the stability of the emulsions themselves. Fingas, et al (2001) have found that water content is not a rigid indicator of stability but they do agree that at levels up to about 50% water content the water is more loosely entrained than chemically bound and the resulting emulsions are more unstable and can be more easily broken. At over 70% water, emulsions tend to be very stable and the oil becomes near-solid, making de-emulsification by dispersants very difficult. Qualitative knowledge of the bound water content before applying dispersants can be helpful in guiding the dispersant response strategy against an emulsified oil. A quick test can be run using demulsifying chemicals to break the emulsion and then visually estimating the relative volume of the water phase. Table 7.1 summarizes the emulsion-forming tendency of various oils, based on in-house emulsion stability tests conducted by ExxonMobil annuitant Ed Shewmaker in the 1970s.

Table 7.1 Relative Emulsifying Tendencies of Crude Oils

Very Strong	Strong	Intermediate	Weak/Very Weak
Arabian Heavy	Agip 100	Alik	Berri
Arabian Medium	Arabian Light	Brega	Brent
Iranian Heavy	Ardjuna	Isthmus	Ekofisk
Iranian Light	Bachaquero	Lagunillas	Flotta
Kirkuk	Basrah	Loolaan	Forties
Kuwait	Cold Lake Light	Murban	Goose Creek
La Rosa	Guanipa	Nigerian Light	Gullfaks
Oman	Hondo	Romashkino	Jay
Sag River	Loudon	San Joaquin	Jobo
Taico	Maya	Sirtic	Mubarek
Tia Juana Medium	Minas	Skikda	Qatar
	North Slope	Suez	Saharran Blend
	Sassan	Zakum	South Louisiana
	Sunniland		West Texas Sour

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More recent studies by Fingas, et al, 1998, 2000, present additional information that can be useful in predicting if a particular oil will form stable emulsions or not. They defined four degrees or “states” of emulsion stability:

Stable – increased viscosity with time due to increasing asphaltene alignment at the oil-water interface

Mesostable – emulsions with properties between stable and unstable, probably comparable to Shewmaker’s “Intermediate” designation in Table 7.1

Entrained Water – water suspended in oil by viscous forces alone

Unstable – decompose rapidly after mixing, generally within a few hours

Using these designations, Fingas, et al, defined the stability of water-in-oil emulsions for over 100 oils. Some of these are summarized in Table 7.2.

Table 7.2 Post-Evaporation Emulsion Stability of Oils (from Fingas, et al, 1998 and 2000)

Stable	Mesostable	Entrained Water	Unstable
Arabian Light	Carpenteria	Belridge Heavy	Bunker C
Arabian Medium	Cook Inlet –Granite Point	IFO 180	Diesel
Cook Inlet – Swanson River	Cook Inlet – Trading Bay	Port Hueneme	IFO 300
Hondo	Dos Cuadras		Jet Fuel
Port Arguello Light	North Slope		Miss. Canyon 72
Sockeye	Prudhoe Bay*		Pitas Point
Sockeye Sweet*	Santa Clara		Sumatran Heavy
Takula	Sockeye Sour*		Tapis
	Waxy Light Heavy Blend*		

** Stability varies with degree of evaporation*

It should be noted that emulsification retards evaporation/weathering and, once an emulsion is broken, the released oil should be more dispersible for a given amount of time passage than it would have been if emulsification had not occurred.

The environmental conditions that influence dispersion are:

- **Sea State.** The most important contributing factor to a successful dispersant application is the amount of energy present. At high sea states (high gale to hurricane force), dispersants are probably not required because the force of the seas alone should naturally disperse most of the oil. Also, spill response activities in very high seas could be unsafe and should be carefully considered. Low to medium seas (ranging from small waves to onset of large waves and light to strong breezes) and high currents favor chemical dispersion. In calm flat seas and at low currents, the oil may not disperse, or if it does, the toxicity impact could be significant because the oil plume will not dissipate as intended and high localized oil concentrations could result.
- **Temperature.** The water temperature affects the competing influences of viscosity of the oil and weathering rate. Low temperature raises viscosity, but the loss of light ends is slower than at higher temperature. The net effect of these factors on dispersion can be

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difficult to predict without the use of models. The warming effect of the sun can also affect dispersibility. On balance, dispersion is likely to be more effective at higher temperature and less at low temperature. This is further discussed in sections 12 and 13.

Salinity. Many of the commonly available dispersants have been formulated to work best in sea water (typically 30,000-35,000 parts per million salt, or as commonly reported, salinity values of 30 to 35 parts per thousand). In waters near winter snow melt or river deltas, salt content could be much lower than in open sea water. At less than 10,000 ppm salt, (10 parts per thousand or less), dispersant effectiveness drops off. Knowledge of the salinity in such areas is an important factor in deciding which dispersant to use in mounting a dispersion response. There are products that are effective in low salinity water and those that have been approved for fresh-water use in France, for example, are: Dasic Fresh Water, Disperep 8, Enersperse 1037, Inipol IPF, Gamlen OD 4500, and Petrotech 25. Corexit products can be made effective in fresh water by adding a bi-valent salt, such as calcium chloride, just prior to use.

7.2 Confirming Effectiveness

The techniques used to monitor the effectiveness of a dispersant application include:

- **Visual Observation.** A spotter aircraft flying at several hundred feet is usually used to confirm that dispersant application is working. Viewing is best when the sun is behind at a 30-55° angle. The initial effect will be for the dispersant to “herd” the thinnest oil (less than 0.01 mm) forming a clear patch of water. On the thicker oil, the dispersant requires some time to diffuse to the interface before dispersion starts to work. Depending on the viscosity and emulsification of the oil, this could take as long as an hour but for most fresh oils the dispersion can occur within minutes and will be evidenced by formation of a colored plume of oil beneath the surface of the water. The most common color seen is a light tan color (see Figure 7.1), though orange and grey have also been observed (Lewis and Aurand, 1997). A light color in the water is a sure sign that dispersion is occurring, as the light is defracted by the plume of small droplets in the water column. However, absence of a visible plume does not necessarily mean dispersion is not happening as the rapid generation of a concentrated plume of dispersed oil droplets and light diffraction is needed for confirmation. According to Lewis, et al, (1995), it may be difficult to see a plume on an overcast day with gray sky and gray sea, as was the case in a 1994 North Sea field test.

The NOAA Dispersant Application Observer Job Aid is a handy guide to use for observing and identifying dispersed and undispersed oil. The guide can be downloaded via <http://response.restoration.noaa.gov/oilaid.html>.

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Figure 7.1 Typical Plume of Dispersed Oil

- **Sampling.** Sub-surface samples can be collected from a boat and analyzed using the proper equipment (Figure 7.2) either on the boat or in the lab. Three levels of depth are commonly sampled to provide a rough profile of oil concentration.
- **Fluorometry.** There are devices based on ultra-violet fluorometry that have been adapted to provide real-time measurement of dispersed oil beneath a treated slick. These fluorometers must first be appropriately calibrated to get more accurate measurements but even uncalibrated results showing relative changes in dispersed oil concentration would be sufficient to confirm that dispersants are effective. Lunel, et al, (1997), used fluorometry to confirm effectiveness and provide net environmental benefit information during the response to the *Sea Empress* spill in 1996. Fluorometry is the key component of the US Coast Guard's SMART (Scientific Monitoring of Advanced Response Technologies) program required to be used to support Federal On-Scene Coordinator (FOSC) decisions in the United States (Henry, et al, 1999).
- **Remote Sensing.** There are as yet no devices available to measure the exact thickness of oil slicks. However, Infra-Red cameras and SLAR (Side Looking Airborne Radar) can detect and characterize oil slicks, so they could conceivably be applied to measure relative differences in thickness and certainly disappearance of surface oil as confirmation that dispersion has occurred.

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Figure 7.2 Sampling in 1997 North Sea Trials

7.3 Laboratory Effectiveness Tests

Numerous laboratory test methods have been developed over the years to evaluate the relative effectiveness of dispersants (Clayton, et al, 1993). Currently six basic test methods, summarized in Table 7.2, are the most common in use at various oil spill research laboratories in Europe and North America. There is as yet no internationally-accepted standard procedure, despite the obvious desirability and benefits of such a test. Government agencies of various countries prefer their own specific standard effectiveness tests for dispersant approval. The test methods use various containers (ranging in size from custom-built tanks to standard laboratory glassware). Mixing energy is generated by a wide range of approaches, including a high velocity air stream, an oscillating hoop, and movement of the test vessels. It is generally possible to vary the energy levels in these tests, as well as the dispersant-to-oil ratio (DOR), settling time, and other variables. Effectiveness is measured as the amount of initial surface oil that ends up in the water phase.

The numerical results of these laboratory tests are useful for comparing dispersants on a relative basis, **but are not representative of actual expected performance at sea**. They all give different absolute results for a single dispersant-oil combination, depending on their energy level. There have been several mis-interpretations of the meaning of lab results, especially in the U.S. More elaborate, mesoscale tank tests have been used to gain better representations of field sea conditions (Daling, et al, 1997; Guyomarch, et al, 1999; Fiocco, et al, 1999b; Belore, 2003). These flume-like tests also provide a convenient means to weather the oil to better represent actual spills at sea. Full-scale field tests are, of course, best for assessing dispersant performance but are very costly and difficult to carry out because of the complex logistics and unpredictable

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weather. Additionally, large scale tests with intentional release into the environment are often met with resistance by government and non-government organizations in many countries.

Table 7.3 Common Laboratory Methods for Testing Dispersant Effectiveness^a

Test	Reference	Energy Source	Energy Rating ^b	Water Vol. (ml)	OWR ^c	Settling Time (min.)	Complexity Rating ^b
MNS	Mackay and Szeto, 1981	High Velocity Air Stream	3	6000	1:600	None	3
IFP-Dilution	Desmarquest et al., 1985	Oscillating Hoop	2	4000-5000	1:1000 then Drops	None	2
Labofina Rotating Flask	Martinelli, 1984	Tumbling Apparatus	3	250	1:50	1	1
Swirling Flask	Fingas et al., 1987	Shaker Table	1	120	1:1200	10	1
Modified Swirling Flask	Venosa, et al.	Shaker Table	2	120	1:1200	?	1
EXDET	Becker, et al., 1991	Wrist Action Shaker	2	250	1:250	None	1

a Modified from Clayton, et al (1993)

b Energy and Complexity Relative Ratings based on eng. judgment: **1 = Lowest; 3 = Highest**

c OWR = Oil-to-Water Ratio (v:v)

Figures 7.3 to 7.6 are photos of some of the dispersant testing equipment used in North America.

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Figure 7.3 Mackay, Nadeau, Steelman (MNS) Test. Energy Provided by Air Stream (Highest Energy)



Figure 7.4 Env. Canada's Swirling Flask Test. Energy Supplied by Shaker Table (Lowest Energy)

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Figure 7.5 US Swirling Flask Modified to Provide Higher Energy and Improve Reproducibility



Figure 7.6 EXDET Test Used by ExxonMobil. Energy Supplied by Rocking (Medium Energy)

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7.4 Large-Scale Wave Basin Tests

During the 1980s and 90s, ExxonMobil conducted numerous significant large-scale tests at its Esso Resources Canada Ltd. Wave Basin in Calgary, Canada. At 55 x 31 meters (181 x 100 ft) this was for many years one of the largest test basins available for oil spill studies (see, for example, Brown, et al, 1985). Tests in this basin routinely achieved oil dispersion, even at low wave energy and low temperatures. This basin is no longer available for oil spill testing but was at its time responsible for many advances in the science of dispersants which under-pin ExxonMobil's longstanding expertise in this field. Thanks to this system, ExxonMobil has been able to confirm dispersant effectiveness over a wide range of treat levels, temperatures, and sea conditions. Some of the significant learnings that resulted from testing at the ExxonMobil wave basin were:

- Dispersants can be effective even if under-dosed at 1:100 or less as long as the oil viscosity remains low.
- Dispersants are effective in brash and broken ice but much of the dispersant will be deposited on ice.
- If dispersants are applied to oil in calm water and wave energy is absent for over a day, the dispersant remains with the oil and can still be effective (Mackay, 1995).
- Lab tests generally under-predict field performance.
- There is enormous dispersing power in a single breaking wave.
- As long as energy is present, dispersed oil droplets will remain suspended in water. When energy is removed, some re-surfacing can occur.

Today, large-scale testing is still possible at the Oil and Hazardous Materials Simulated Environmental Test Tank (OHMSETT) wave basin in Leonardo, NJ, thanks in large part to the long-term commitment to oil spill response over many years by the US EPA and the Minerals Management Service. OHMSETT is an outdoor tank 203m long by 20m wide and 3.4m deep holding almost 10 million gallons of sea water. This facility has provided detailed characterization of oil dispersion for numerous oil types and weathering conditions over a wide range of environmental temperatures and wave conditions (Belore, 2003, Ross and MAR, 2006) confirming the expectations that dispersants can be effective under most spill response circumstances (see photo of test on ANS crude in Figure 7.7).

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Figure 7.7 Dispersant Test on ANS Crude at OHMSETT

7.5 Large-Scale Field Tests

Dispersant field tests have been sporadically carried out in open water with full regulatory approval since the mid-1970s with the U.K., Norway, and (until the 1990s) Canada being the leaders in allowing such tests. The United States allowed open sea testing for a short time during the late 1970s to early 1980s but has been reluctant to permit it since then. The US EPA says that it supports open sea oil tests, but the approval process is very involved and no permits have been issued for the past 25 years. In 1989, the U.S. National Research Council assessed the results of all field tests carried out up until that time and concluded that “in a few carefully planned, monitored, and documented field tests, as well as in laboratory tests, several dispersants have been shown to be effective—that is, they have removed a major part of the oil from the water surface when properly applied to oils that were dispersible” (NRC, 1989).

Under well-characterized operational conditions, dispersant field tests have been quite successful. In actual applications to real spills, however, results of dispersant operations to combat oil spills have been mixed (Steen and Findlay, 2008). This underscores the importance of proper pre-planning and use of knowledgeable advisors who understand the many variables that affect dispersant performance and the limits of effectiveness. The most recent large-scale field test was carried out in the UK North Sea in 1997. This test focused on dispersibility of weathered crudes and heavy oils, which is discussed in the next section.

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8.0 DISPERSION OF HEAVY VISCOUS OILS

The previous sections have discussed the notable benefits of dispersant use in response to oil spills. Like all response strategies, dispersants may have limitations as a result of logistical, temporal or environmental issues. One of the first considerations in the immediate aftermath of an oil spill was succinctly stated by Lewis (2003): “Will the dispersant ‘work’? (Will spraying dispersant cause the spilled oil to be rapidly dispersed under the prevailing conditions?).” Much research has been carried out to try to obtain a standardized answer to this question and many scientists have attempted to establish definite parameters for dispersant use for a variety of conditions. One of the main issues that remains unclear is the maximum oil viscosity at which dispersant use will be successful under actual environmental conditions. This has proved to be one of the most complex issues to understand and explain.

Traditionally, it has been believed that dispersants are ineffective on oils above a certain viscosity. In 1987, the International Tanker Owners’ Pollution Federation (ITOPF) stated that “...as viscosities reach the region of 5000-10000 cSt, [dispersants] are ineffective...” This may have been the case for early dispersant formulations. For example, in 1978 the *Eleni V* was involved in a collision with the *Roseline* off the South Coast of England resulting in a 7500 tonne (47,000 bbl) spill of 5000 cSt (≈ 5300 cP) heavy fuel oil. Some 900 tonnes (5700 bbl) of BP1100 and Dasic LTSW were applied without any dispersant effect (Nichols, et al, 1985).

Over the past 30 years, however, extensive research into dispersant effectiveness has been carried out by governments, industry and independent bodies resulting in the development of improved dispersants that possess lower toxicities than their predecessors yet, in many cases, are far more effective. This is believed to be due to higher surfactant content in many new formulations. Contrary to earlier thinking, the new dispersants, in many instances, have proved to be very effective at dispersing highly viscous, weathered and emulsified oils that were previously believed to be un-dispersible. Following research carried out at the “Polludrome” (wave basin) at Le Cedre in Brest, France, Guyomarch, et al, (1999), stated that “...oil viscosity limits for dispersion, which had been defined in the eighties, can be upgraded to reflect the improvements made in the formulations of the modern dispersants.” This conclusion is further strengthened by research carried out in 2000 in a large wave basin at SL Ross in Ottawa, Canada with the newer formulations. For example, the experiments revealed that Bunker C fuel oil with viscosities of 2000-7800 cP could be dispersed with an effectiveness of between about 69 and 97% using dispersant-to-oil ratios of 1:20, 30 and 40 (SL Ross, 2000).

The research by SL Ross serves as one example of the extensive work carried out at sea, in wave basins or laboratory experiments by a number of scientists that has challenged the theory that there is a fixed viscosity cut-off for effective dispersion. The data, however, are not straightforward, partly because viscosity is not the sole parameter of importance in determining the dispersibility of oils. Many other variables have a direct influence, as indicated below, and any or all of them can mask or confuse the role of viscosity:

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- **Wave energy** – generally the higher the energy, i.e., frequency and magnitude of the waves, the greater the speed and effectiveness of heavy oil dispersion.
- **Wind speed** – this is linked to wave energy but speeds of 5-25 knots are optimal for effective dispersion (ITOPF, 2005).
- **Surfactant content** – the higher the quantity of surfactant, the better the chance of pulling large hydrocarbon molecules present in the bulk oil into the small dispersed oil droplets. However, surfactant concentration varies greatly among products, and thus assessments of dispersibility of heavy oil can be product-dependent.
- **Solvent type** – oil soluble solvents will latch onto the oil molecules more readily than water soluble solvents, again raising the importance of product formulations.
- **Oil concentration** – if the oil spreads into a continuous slick of constant thickness the dispersion will be far more efficient.
- **Dispersant-to-oil ratio** – the higher the proportion of dispersant molecules to oil molecules, the more rapid and effective the dispersion.
- **Oil chemistry** – the types of molecules that make up the oil, i.e., size, complexity, etc., will determine the potential for dispersion. Very large hydrocarbon molecules are more likely to be dispersible in the presence of smaller solvent molecules that can help pull them into the water phase as they themselves are dispersed. In this case, the dispersant solvent can play a very vital role in enhancing the dispersibility of heavy oil.
- **Temperature** – lower temperatures not only increase the viscosity of oil but can also slow the reaction between dispersants and oils by reducing the diffusion rate of the surfactants. Low temperatures may, however, reduce the rate of evaporation of the light ends maintaining a lower viscosity for longer periods.

In many experiments, adjusting just one of these variables can dictate whether dispersion will be successful or unsuccessful. **Many of these variables cannot be controlled in a real spill environment; thus, it is very difficult to predict the extent to which a dispersant will be successful without testing it in the specific conditions present at the time of the spill.**

8.1 Issues and Interest in Dispersing Heavy Oils

There are many reasons for the recent interest in dispersing heavy, viscous oils. These are discussed fully below.

8.1.1 Ecological Damage Caused by Recent Heavy Oil Spills

Dispersion of heavy oils has risen in importance over recent years due to several heavy crude and heavy fuel oil spills which resulted in severe consequences for sensitive coastal environments, for example, the *Erika* spill in 2000 and the *Prestige* spill in 2002, both in waters off Europe. It is generally accepted that heavier oils do not have the same toxic impact on water column organisms as lighter oils do because the larger molecules are minimally soluble and cannot penetrate organisms in the same way. Their smothering tendencies and persistence, however, can

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pose a longer term environmental threat once they strand on shorelines and inflict direct and sub-lethal effects that over the long term, may be more severe. For example, the insulation and water proofing tendencies of many birds and animals may be affected by contact with heavy oils, reducing their ability to forage successfully and leading to malnutrition of juveniles. The persistence of heavy oils on shorelines can result in a slow, continuous release of hydrocarbon components into the environment over many years, impeding rapid recovery of the region.

The ability to disperse heavy oils offshore to avoid a coastal impact would prevent the direct and longer-term shoreline damage mentioned above as well as being a less intrusive, faster and lower cost overall clean-up method (Suidan, et al, 2005). Dispersing heavy oil would generate a trade-off for consideration as it could cause other different types of ecological impacts at sea. However, as discussed in the next section, the effects would be much shorter lived due to rapid dilution of the dispersed oil, ability of fish communities to move out of the affected areas and the high fecundity of offshore communities (IPIECA, 2000). As discussed in the section on NEBA, recovery rates for populations of bird species and higher mammals are very much slower than water column organisms; it can take years for affected wildlife populations to return to pre-spill levels.

8.1.2 Emulsions & Oil Composition

Much research has been carried out on heavy crudes and heavy fuel oils (HFOs) to evaluate whether they would be amenable to dispersion. Heavier crude oils may have a greater propensity to emulsify due to the higher asphaltene content in many instances (Baker, 2003). The greater the asphaltene content, the more rapid and stable the emulsification process. While it was previously believed that emulsions cannot be dispersed, several of the new dispersant formulations actually break the emulsion and then facilitate dispersion. This can be a slow process and may require multiple dispersant applications—firstly with a very low dosage to break the emulsion then at a higher dosage to induce the actual dispersion. Alternatively, a demulsifier can be applied followed by a dispersant, although compatibility between the two substances must be ensured (Guyomarch, et al, 1999). Most crude oils purchased for transit to a refinery undergo chemical profiling prior to loading to document the content and levels of such molecules within the oil. If the type of crude and its specific chemical characteristics are known early on in a spill, better predictions of dispersibility may be deduced.

HFOs present a more difficult problem when assessing dispersibility. Research on dispersing HFOs has been very positive in some experiments but, in others, using the same variables and apparently the same HFO, the results have been very different. It is possible that this is a result of the HFO chemical composition. These products generally are the remnants of the refining process after removal of the lighter molecules and are categorized and sold by their viscosity properties alone, i.e., an IFO 380's only requirement is that it have a viscosity of no more than 380 cSt ($\approx 400\text{cP}$) at 50°C. Refineries use a variety of different crude oils as feedstock; thus, the chemical composition of a specific grade of HFO can vary significantly from batch to batch and from refinery to refinery. As previously mentioned, a change in asphaltene, naphthalene or wax

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content can have a marked effect on the dispersibility of a spilled oil (Strøm-Kristiansen, 1997); thus, it cannot be said that all IFO 380s are or are not dispersible. Viscosity can, in fact, be a misleading parameter on which to solely base any dispersion decision.

8.1.3 Other Available Clean-Up Options

Heavy, weathered and emulsified oils do not only pose a problem for dispersants but are notoriously difficult to clean up by mechanical means, such as with pumps and skimmers. Many pumps cannot move oils of high viscosity and heavy oils do not have the same oleophilic properties as medium to light oils; so viscous HFOs are not amenable to many types of disc, brush and drum skimmers. Many of the heavy oils are also quite dense, approaching the specific gravity of the sea water and can become neutrally buoyant. After time at sea these oils become weathered and emulsify and can also be exposed to sedimentation, i.e., entrainment of sediment particles, which makes them even heavier and potentially prone to sinking and/or suspension below the surface. Unfortunately, in many heavy oil spill situations, the only way to capture the oil is to recover it after a shoreline impact. This is highly labor intensive, poses a greater health and safety risk, can generate up to ten times the oil volume in waste than an at-sea response (IPIECA, 2004) and is very costly both in time and money. Effective dispersion would alleviate many of these issues.

8.2 Research Results

The problems of heavy oil spills and, particularly, the lack of feasible response options have led to a plethora of dispersant research stretching from the early 1990s to the present day. Research has been carried out on a very wide range of crude oils including Alaska North Slope (ANS), California Outer Continental Shelf (OCS) and Hibernia as well as heavy fuel oils including IFO 180, IFO 380 and Bunker C to assess amenability to dispersants. The results and success rates vary greatly due to a wide variety of testing protocols, oil composition, dispersant application ratio and dispersant composition, to name but a few. Section 7 and, in particular, Table 7.2 describe various testing methods fully. One of the main differences between the tests is the level of energy employed to induce dispersion. Because the role of dispersants is to reduce the interfacial tension between oil and water, heavy oils are much more likely to disperse with high energy levels after dispersants have somewhat reduced base interfacial tension.

It has generally been assumed that there would be a link between heavy oil dispersibility and the oil's density when analyzing dispersant effectiveness. However, the use of density can be very misleading as can be seen from Figure 8.1 on the following page, which shows results from 16 independent studies in Norway, the US, Canada, and the UK. This plot shows a wide range of results without obvious positive correlation with either crude or fuel oils.

It would be expected that oils of a lower API gravity (i.e., the denser oils) would show lower dispersant effectiveness. This, however, is not the case for all data. In ExxonMobil tests using the EXDET apparatus, some oils of just over 10° API (only 1-2 degrees less dense than bitumen) have shown dispersant effectiveness of over 90%. Other points in Figure 8.1 show much less dense oils of approximately 16° API having a dispersant effectiveness of less than 10%. Out of

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the 345 tests plotted on the graph, over a third of the heavy oils show dispersant effectiveness percentages of over 60% no matter what the API gravity. This illustrates the poor correlation between specific gravity (i.e., density) and amenability to dispersion when disparate testing programs are compiled, indicating that specific test variables need to be taken into consideration when attempting to predict dispersant effectiveness.

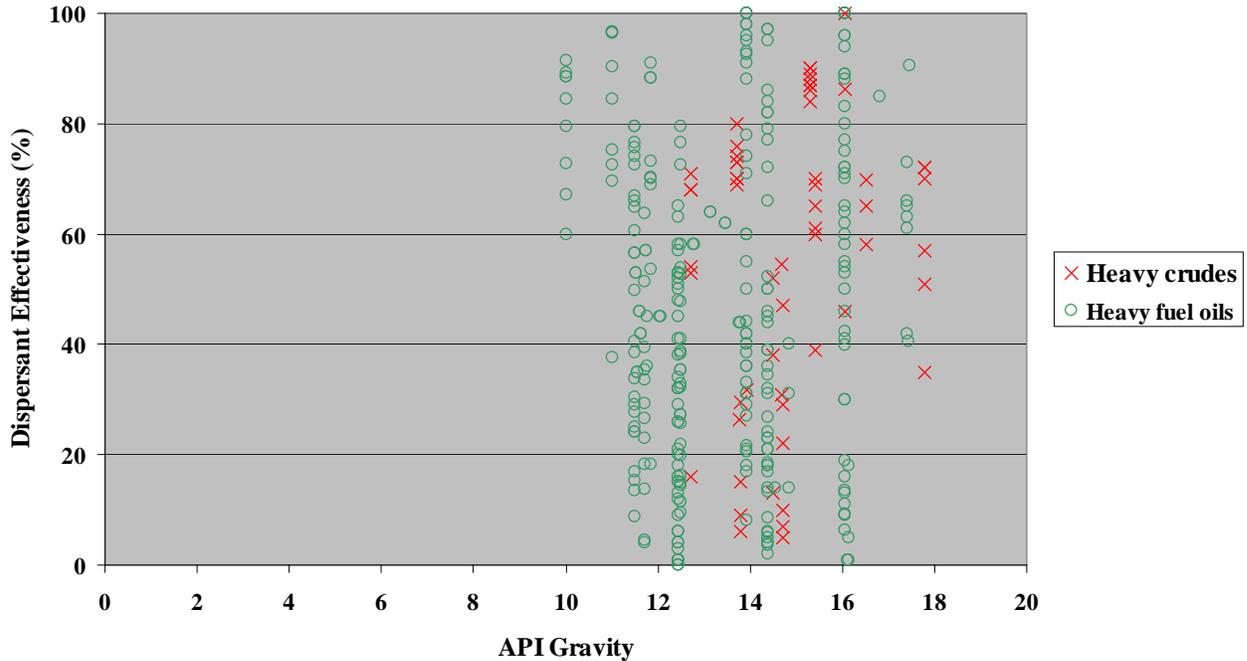


Figure 8.1 Plot Comparing Percent Dispersant Effectiveness for Heavy Crude Oils and Heavy Fuel Oils of Various API Gravities Using Different Test Methods

A better link between oil viscosity and dispersibility is illustrated in Figure 8.2. As expected, more viscous oils are generally less dispersible than lighter oils. The information illustrated in Figure 8.2 also benefits from being obtained from a single set of research data. Since the data came from the same testing protocol (EXDET) under the same conditions, as opposed to the multiple data sets represented in Figure 8.1, they are assumed to be more internally consistent and amenable to analysis.

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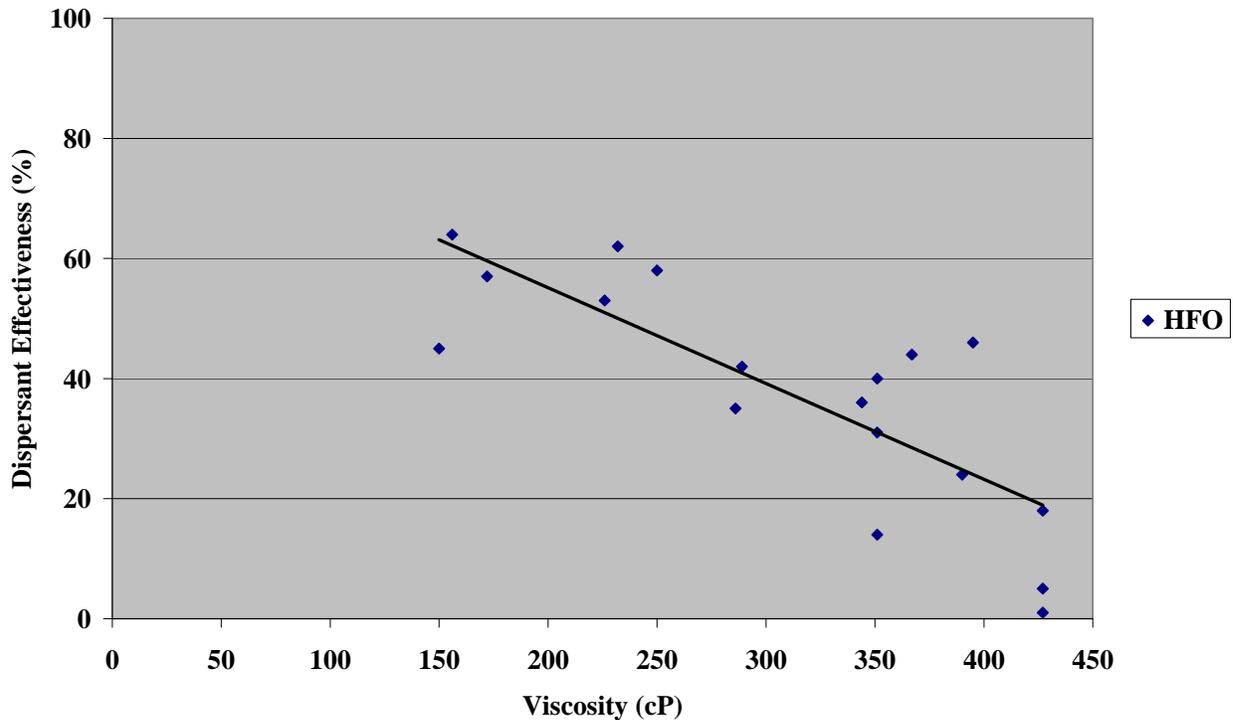


Figure 8.2 Plot Comparing Percentage Dispersant Effectiveness for Heavy Fuel Oils of Various Viscosities Measured at 50°C (from Fiocco, et al, 1999)

Figure 8.3 again shows a correlation between dispersant effectiveness and oil viscosity. As in Figure 8.2, this correspondence between effectiveness and viscosity is clearer when only one data set is included. In this instance the research was carried out in a large outdoor test tank (Ohmsett) exposing the experiments to more 'real' uncontrolled conditions, e.g., ambient air and water temperature, wind, dilution extent, etc. This shows that dispersants can be unexpectedly effective on heavy oils outside laboratory conditions.

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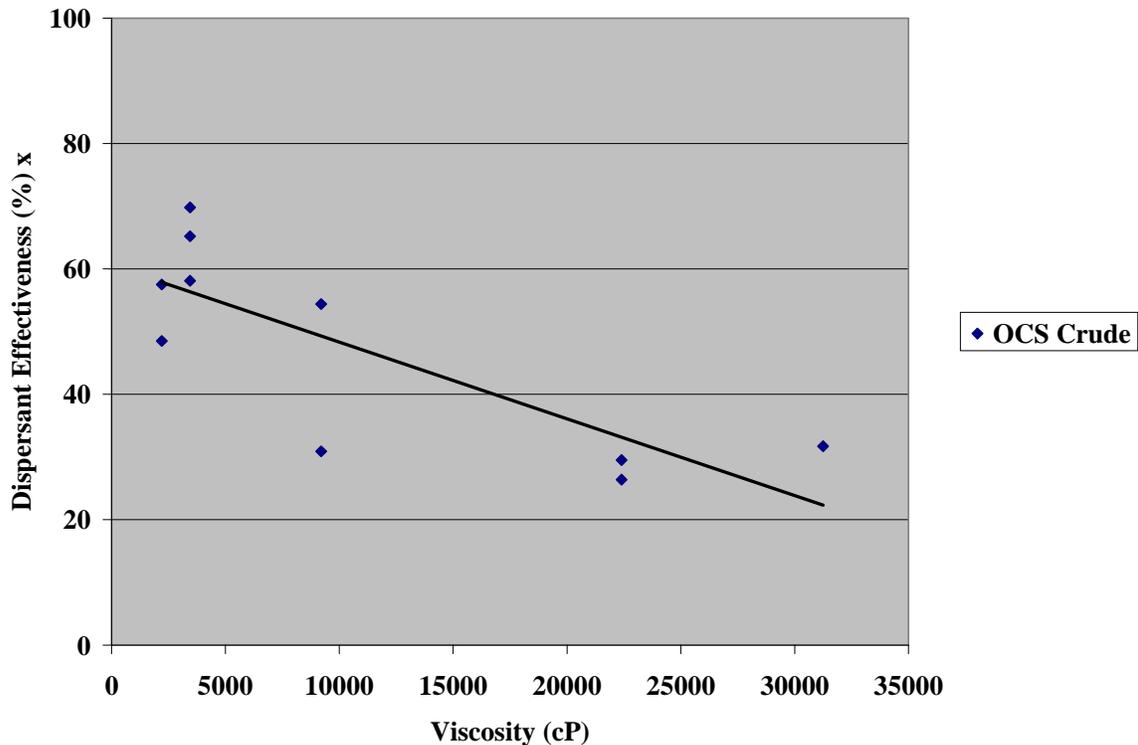


Figure 8.3 Plot Comparing Percentage Dispersant Effectiveness for Outer Continental Shelf (OCS) Crude of Various Viscosities Measured at 15°C (from Ross and MAR, 2006)

Another variable affecting the data in Figure 8.1 is that many dispersant-to-oil ratios (DORs) were included, ranging from 1:5 up to 1:150. It is generally accepted that, the smaller the number of parts of oil to each part of dispersant, the greater the chance of dispersion. This is especially true in the case of heavier oils as dispersant can be washed off during the extended time period that it takes for the surfactant to penetrate the oil. A higher ratio gives a better chance of more of the dispersant remaining on and penetrating into the oil so that dispersion may be successful.

Variable DORs were used in the SL Ross and MAR, Inc. 2006 research. Figure 8.4 shows the DORs for each specific data point in the aforementioned data set.

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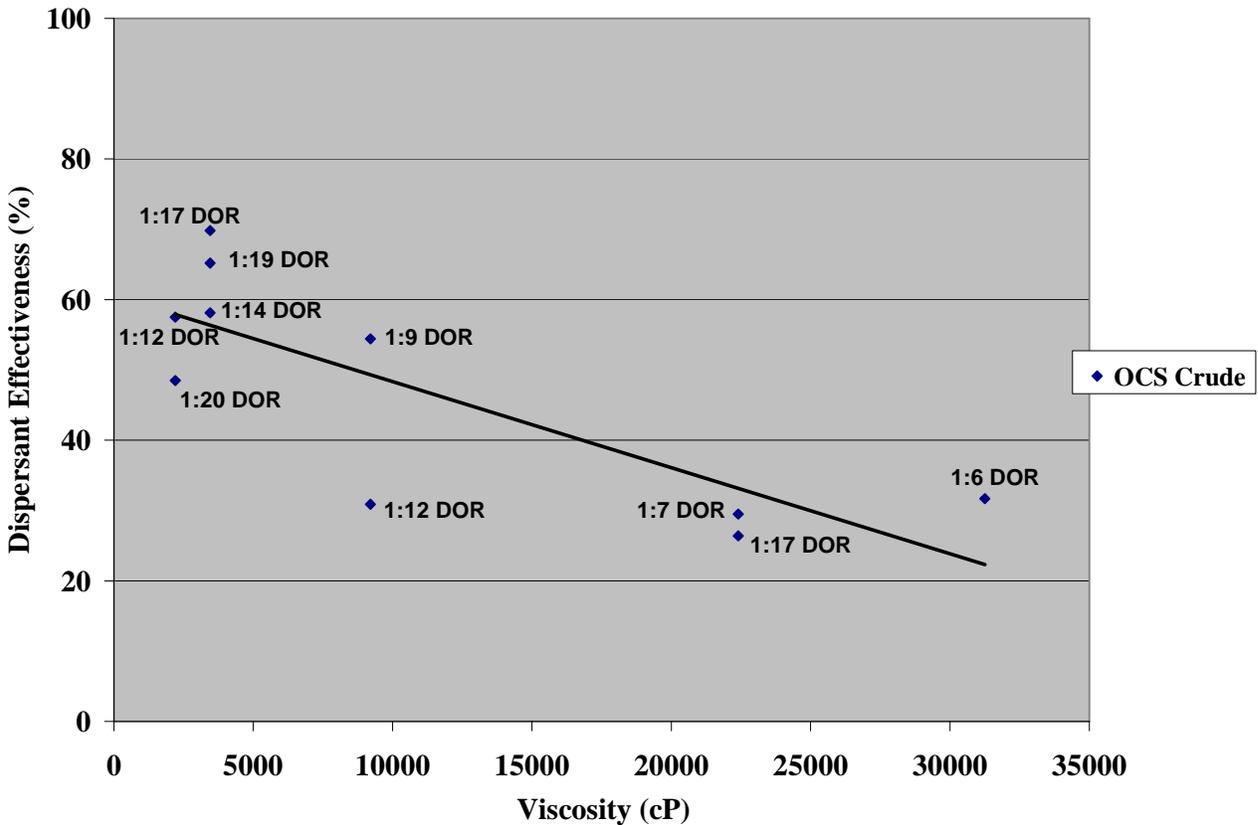


Figure 8.4 Plot Comparing Percentage Dispersant Effectiveness for Outer Continental Shelf (OCS) Crude of Various Viscosities Measured at 15°C (with DORs shown) (from Ross and MAR, 2006)

Unexpectedly, this plot shows little correlation between the application rate of dispersant and the percentage dispersant effectiveness at a given oil viscosity. This may be due to the ‘real’ nature of the trials in that the amount of dispersant actually making contact with the oil may not match the amount that was applied to the slick due to wind drift and other environmental factors. In order to maximize the possibility of the dispersant remaining in contact with the oil and thus maximizing its effect, it was recognized that new dispersant formulations were needed. These dispersants utilize a more oil-soluble solvent to carry the surfactant so that the potential for the dispersant to be washed off the oil has been reduced. There are many other factors that can affect oil characteristics and the resulting performance of dispersants, both in laboratory tests and real spill situations such as those discussed below.

As the oil industry has moved into colder regions of the world, e.g., Alaska, Sakhalin, Caspian Region, etc., the probability of oils being spilled into cold environments has increased. In order to mitigate the effects of working in a cold climate and increase ease of handling, many heavy oils

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are transported at an artificially high temperature to maintain a low viscosity. Not surprisingly, heavy oils at high temperatures behave similarly to naturally light oils. However, if a heavy oil is spilled into cold water or ice, the viscosity will rise rapidly, and response options will be quickly limited. This may affect the amenability to dispersion. With this in mind, Belore (2002) carried out a series of experiments on Hibernia crude at the Ohmsett wave tank facility in New Jersey, to see how temperature affected dispersibility before oil reached its pourpoint limit.

For this study, the water temperature was set at 1°C and the oil was tested in a fresh state and then evaporated by 9.2%, 12.3% and 27.6% to simulate weathering. DORs ranged from 1:13 up to 1:116. The results showed that dispersant effectiveness on fresh and 9% evaporated (i.e., 9% weathered) crude ranged from 85-100% and it was concluded that they had not been affected by the cold temperatures. One reason that oils may remain dispersible at lower temperatures is that the rate of evaporation of the light ends will be reduced enough that their retention will help balance the thickening effect of decreased temperature. As a result, the overall viscosity will remain low and leave the oil amenable to dispersants for a longer period of time. However, the rate of dispersion will also be slower. The more heavily weathered oils (12.3% and 27.6% evaporated), on the other hand, were less successful with dispersant effectiveness, results ranging from 40% down to 0%.

As previously discussed, experimental conditions, whether in a flask or a wave tank, are generally unrepresentative of a real spill. Conditions cannot be controlled in the same way in an actual spill situation. For example, toxicity levels remain deceptively high in the closed systems usually encountered with flasks and tanks due to a lack of dilution potential. It is also thought that there may be artificially high mixing energy that results when the oil-dispersant mix collides with the flask or tank wall. Surprisingly, Trudel, et al, (2005) found that the Swirling-Flask Test (SFT) actually produced artificially low dispersant effectiveness results, i.e., oil dispersed more easily at sea than in the flask. In general, it must be remembered that, while many of the experimental methods are essential for a comprehensive study of dispersant mechanics and a relative understanding of dispersant performance, they cannot accurately predict or simulate conditions during an actual spill event.

8.2.1 North Sea Field Trials

To test these issues and to get a better feel for real conditions, a series of sea trials were conducted in the UK in 1997, co-funded by British and American governmental bodies, ITOPF, SINTEF, and several oil companies. Four large slicks of oil were laid down in the North Sea 30 miles off the coast of England: two of Forties blend crude (50 tonnes each), one of Alaska North Slope (ANS) crude (30 tonnes) and one of IFO 180 (20 tonnes) (See Figure 8.5). The crude oils were left to weather and emulsify for two days and then sprayed with dispersant from an aircraft. In the ANS test, which is most relevant to this section, the crude oil was weathered at sea for 55 hours, attaining viscosities ranging from 15,000 to 20,000 cP (measured at 15°C and 10 sec⁻¹). Upon application of Corexit 9500 dispersant, the surface emulsion broke immediately (Figure 8.6) and monitoring equipment indicated elevated dispersed oil concentrations over a large

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volume of the subsurface sea (Lewis, et al, 1998; Lessard and DeMarco, 2000). This demonstrated that, for weathered and emulsified crude oils, dispersants can be a feasible response option even after a 55 hour delay.

Corexit 9500 was then applied to IFO-180 that had weathered for 4.5 hours at sea. The viscosity of the IFO-180 was approximately 6,000 to 8,000 cP. The average dispersant-to-oil ratio (DOR) was 1:44, less than the intended dosage rate. Only partial dispersion of the emulsified IFO-180 was achieved at the low DOR, probably due to under-dosing. Logistical problems delayed timely additional dispersant application. Consequently, IFO-180 remaining on the sea surface continued to emulsify while the viscosity increased. Corexit 9500 was applied again at approximately 23 hours. Some dispersion of the IFO-180 occurred, but subsurface concentrations of oil remained low. It was concluded that emulsion with a viscosity less than approximately 20,000 to 30,000 cP had been dispersed, but emulsion with the higher viscosities was not dispersed.

The field trials showed that dispersants can in some instances be effective on highly viscous crude oil and IFO-180 emulsions. Prior to these North Sea trials, IFO-180 had been considered not dispersible. The trials also showed that the time window for Corexit 9500 can extend for two or more days following a crude oil spill. These data again show that the current viscosity cut-off predictions of around 10,000 cSt or approximately 10,500 cP (ITOPF, 2005) should no longer be the main limiting factor in deciding to implement a dispersant response, but demonstrate that weathering and emulsification do have a major influence and need to be considered as part of overall decision-making.



Figure 8.5 Slicks in the 1997 North Sea Trials Were Extensive. Oil is in the Bright Area.



Figure 8.6 ANS Emulsion Dispersing After Chemical Application in the 1997 Trials.

8.3 Conclusions Regarding Heavy Oil Dispersion

The wide range of research that has been carried out so far in this area is fairly inconclusive with respect to a simple answer regarding a viscosity limit for successful dispersion. Some heavy oils have been shown to readily disperse where others with similar compositional characteristics have not. It is not simply the viscosity of the oil, as previously thought, that determines dispersibility but an array of factors including mixing energy, sea temperature, weathering, chemical composition, dispersant formulation, and dispersant dosage. The effects of wave energy are illustrated by SL Ross, et al, 2005:

“While the at-sea tests suggest that an oil with a viscosity of 7000 cP may limit the dispersibility under some conditions, both at-sea and Ohmsett tests suggest that this limitation may be overcome by increasing the mixing energy. Indeed the Ohmsett results suggest that in the 33.3 cpm waves the limiting viscosity may lie between 7,100 and 19,000 cP. Operationally, this means that despite the evidence for oil viscosity limiting dispersion of IFO 380 at sea in winds of 7 to 10 knots, oils of 7000 cP or greater may indeed be dispersible if the level of mixing energy is high enough.”

The overall conclusion is that many heavy oils may be amenable to dispersion under a certain suite of conditions. Thus, in the event of any heavy oil spill in the appropriate

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situation and with the consent of statutory bodies, it would be prudent to carry out a field test immediately to show whether dispersants might be effective and preclude a premature decision of dispersants being arbitrarily and unnecessarily excluded. The cost of such a test may be trivial, if dispersants are shown to be effective, in comparison to the potential enormous cost of shoreline cleanup and remediation if dispersion is not applied. As a reminder, the cost impact of the cleanup for the *Prestige* spill was over 1 billion USD (see Case Studies below).

8.4 Case Studies

The following case studies have been selected to show the variation in success of dispersant application on heavy oils.

MT *Evoikos*, 15th October 1997

The vessel was involved in a collision with another tanker in the Strait of Singapore spilling 29,000 tonnes of HFO. Approximately 500 tonnes of dispersant were applied to the spill by vessel-mounted systems as aircraft were not permitted to fly over the busy shipping channel. The oil was initially dispersible due to moderate viscosities and high ambient temperatures; however, weathering processes increased with time preventing further dispersion compounded by a lack of mixing energy. Thereafter, mechanical recovery was employed (Dicks, et al, 1998). This example proves that immediate action is required if dispersants are to be used on heavy oils due to the very small window of opportunity. Dicks, et al, state that “High oil viscosity was the main factor limiting dispersant effectiveness.”

Freighter *Blue Master*, 27th August 1999

The vessel was involved in a collision with a shrimp boat resulting in damage to the hull and a spillage of 110 bbls of IFO 180. The slick rapidly spread to 3 x 5 nautical miles so dispersants were employed immediately even though there was skepticism among some regulatory representatives as to the effectiveness of dispersants on such an oil. Seven hundred gallons of Corexit 9500 were applied at a target application ratio of 1:10 and observers noted some immediate dispersion although most of the dispersion was very slow due to a lack of mixing energy. By the next morning, only sheen remained. Some tarballs washed up on shore a few days later but this took only hours to clean up and represented only 2% of the amount of oil spilled. The minimal damage to the coast was accredited to the successful application of dispersant at an early stage (Henry, 2005).

MV *Prestige*, 13th November 2002

The tanker *Prestige* got into distress off the coast of Spain on 13th November, 2002 during heavy seas. The vessel eventually broke in two on 19th November spilling an estimated 63,000 tonnes of her cargo of HFO. After discussion among authorities and responsible parties, it was deemed that dispersants would not be able to disperse the oil so no field trials were attempted. Mechanical response commenced at sea utilizing purpose built response vessels from nine different countries with side-sweep collection systems. The oil, however, still reached the coast

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contaminating 1900 km of Spanish, French and British shores. The cost of the manual clean up that ensued, involving 5000 military and volunteer workers, together with compensation claims, totaled €1bn with a further cost of €1m for removal of the remaining oil from the wreck. One hundred forty-one thousand tonnes of oiled waste from the shoreline response still remained to be treated at the time this manual was prepared. If a test spray of dispersant had been carried out successfully, even if only partially, the scale and cost of the resulting response might have been greatly minimized (ITOPF 2004 and IOPC 2006).

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9.0 TOXICITY CONSIDERATIONS

9.1 General Overview

Toxicity is the inherent ability of a substance to cause harm. All substances have this ability to some extent, but in some cases it can occur only at extremely high doses. As Paracelsus (1493 – 1541), the recognized father of modern-day toxicology, proclaimed five centuries ago:

*“ All substances are poisonous; there is none which is not poison.
The right dose differentiates a poison from a remedy.”*

In other words, too much of anything, even well-known remedies such as aspirin or sleeping pills, can be harmful. The same rationale applies to dispersants and dispersed oil. The key determinants of toxicity for a given species are concentration and time of exposure, which can be expressed as follows:

$$\textit{Toxicity} = f(\textit{concentration}, \textit{contact time})$$

Some oil spill scientists have actually combined concentration and time of exposure into a parameter, **ppm-hr**, that facilitates comparisons of overall exposure to dispersants and dispersed oil among different data sets (IPIECA, 1993). However, there is no current, simple approach for assessing chemical exposure and toxic effects that provides a reliable, accurate means to predict the impact of oil spills and response actions on the diversity of marine species over a range of environmental conditions in oil spill response situations. Thus, assessments of potential impacts of dispersants and dispersed oil rely on specific laboratory test constructs plus extrapolations to likely field conditions.

The primary goal in chemically dispersing oil into the marine environment is to rapidly reduce both the oil concentration and exposure time to levels well below those that are required to exert toxic effects. This is achieved through dilution in the receiving water. Laboratory toxicity tests have shown that toxic impacts can require considerable exposure time to occur, up to several days for some species, at typical concentrations of dispersant and dispersed oil measured in the water column following successful oil dispersions. However, in actual dispersant applications, oil concentrations have been shown to drop to very low levels (i.e., below 1 ppm) in less than a few hours. The degree of sea energy plays a significant role in determining the rate at which effective dispersion is achieved.

9.2 Toxicity Testing of Dispersants

Standard laboratory tests are used mainly to establish relative toxicity of dispersant products. However, these common laboratory tests greatly overestimate the potential for toxicity under real-world conditions because laboratory concentrations and exposure times are very conservative and do not properly reflect the transient conditions in the field water column. In most standard tests, organisms are exposed to a constant concentration of dispersant or dispersed oil for as long as 96

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hours. While useful for generating comparative data, this does not accurately reflect what happens at sea.

During the 1960s through the 1980s, many conclusions with regard to potential toxic effects of dispersant and dispersed oil in the field were based on results from conservative multi-day, static, constant-concentration tests. There was no realistic toxicity methodology available that could better simulate the actual conditions of the marine environment where oil and dispersant concentrations are known to decrease continuously. The standardized static tests, that had been developed decades ago for product comparisons or for application to fairly constant effluent streams, were utilized because they were the only tests available at the time.

As in the case of dispersant effectiveness, there is no single international standard test for measuring dispersed oil toxicity to marine biota. The methodology varies widely. Table 9.1 on page 70 is a simplified summary of toxicity test methods used in various countries, modified from Pauwels and Clark, 1993. A variety of test species is used around the world, since each country prefers to test those that are indigenous to that region. Some countries prefer methods that evaluate the dispersant effect alone, while other countries employ methods that compare chemically dispersed and physically dispersed oil without quantifying exposure conditions.

Some tests use 2 day exposures, while others use 4 day exposures. Others use tests that are based on short chemical exposures (< 2 to 6 hours) followed by observation during 1-3 days of recovery in clean water. The short exposure tests do assess effects under more environmentally realistic exposure conditions, but unrealistically high concentrations of dispersant are frequently needed in order to detect an adverse effect during the short exposures. For example, the UK sea test uses 100 and 1000 ppm of dispersant and oil, respectively. The need for such high concentrations to observe adverse effects at short exposure times underscores the relatively low acute toxicity of current dispersant formulations in real-world conditions.

In the last 15 years, thanks in large-part to an impetus provided by the Marine Spill Response Corp's (MSRC) R&D program in the early 1990s, partners in that program, led by state R&D organizations in Texas and California, addressed the issues of static tests not being relevant to the marine environment and severely over-predicting actual field impacts. As stated earlier, dilution and mixing in the field reduce exposure concentrations to very low levels within hours. The MSRC program resulted in broad application of a transient test that can evaluate dispersed oil impact much more realistically than its static predecessors. This test, developed by the University of California at Santa Cruz, involves a spiked declining exposure, and is commonly referred to as "the California Test" (Singer, et al, 1990).

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Table 9.1 Summary of Dispersant Toxicity Tests for Selected Countries

Country	Species	Test Material ¹	Exposure Duration
Argentina (in early 90s)	brine shrimp	D, DO, O	2 days
	fish	D, DO, O	4 days
Australia	amphipod	D	4 days (up to 7 days if needed)
	banana prawn	D	
	isopod	D	
	reef mullet	D	
Canada	rainbow trout	D	4 days
France	brown shrimp or white shrimp	D	6 hrs and 1 day recovery
Hong Kong	rabbitfish	O, DO	100 min and 1 day recovery
	sea urchin	O, DO	100 min and 1 day recovery
Indonesia	tilapia	D	4 days
Japan	medaka	D	1 day
	diatom	D	7 days
Malaysia	tilapia	D	2 days
Norway	brown shrimp	O, DO	100 min and 1 day recovery
	limpet	O, DO	6 hr and 3 days recovery
	green alga	DO	4 hr
Republic of South Africa	sand shrimp	O, DO	100 min and 1 day recovery
Singapore	glass fish	DO	4 days
United Kingdom	brown shrimp	O, DO	100 min and 1 day recovery
	limpet	D, O	6 hr and 3 days recovery
United States	silverside	D, DO, O	4 days
	mysid	D, DO, O	2 days

¹O: Oil; D: Dispersant; DO: Dispersed Oil

In the California test, dispersant is added to the test chambers followed by introduction of organisms. Sea water is then immediately pumped through the test chambers, gradually flushing the dispersant (or dispersed oil) from the system. Figure 9.1 shows the design and a picture of the

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test chamber, which is about 10 cm wide, allowing for tests of the most sensitive, early life stages of many marine species. The decreasing concentrations are measured until they fall below detection limits, which typically occurs within 4 to 6 hours, comparable to measured field data. Several academic and industry research labs, in addition to the State of California, now use the spiked, declining exposure test to measure dispersant toxicity. It is also the basis of approval testing in New Zealand. ExxonMobil advocates its adoption and use for assessing potential effects of dispersants and dispersed oil.

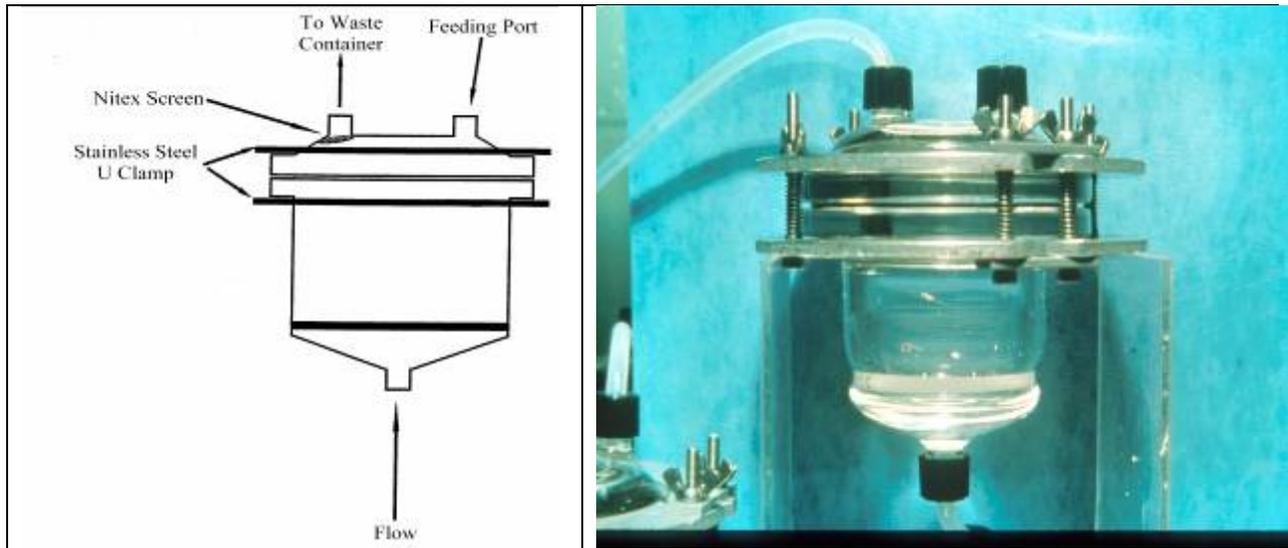


Figure 9.1 "California Test"

9.3 Dispersant Toxicity

Aquatic toxicity for short-term exposures is described using LC_{50} (Lethal Concentration) and EC_{50} (Effect Concentration) endpoints. The LC_{50} is the concentration that causes acute mortality in 50% of test organisms in a specified time period (usually 48 or 96 hours). The EC_{50} is the concentration causing a specific non-lethal effect (such as reduced growth or immobility) in 50% of test organisms in a specified time period. The greater the LC_{50} or EC_{50} value, the lower the toxicity; that is, a higher concentration is required to produce a specified adverse effect. LC_{50} and EC_{50} values are not absolute, but are a range of values for each species and set of test conditions. The range in LC_{50} values results from biological and laboratory variability (George-Ares and Clark, 2000).

An important determinant of aquatic toxicity is chemical composition. As mentioned earlier, the 1967 *Torrey Canyon* spill was the first notable application of chemicals to treat a crude oil spill. The products used were degreasing agents containing as much as 60% aromatic solvents. These degreasing agents had been developed for cleaning oily residues from tanker compartments and were not originally intended for use in cleaning up oil spills in the marine environment. The

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result of their use was extensive mortality of marine organisms. This experience prompted the subsequent development of formulations specifically intended for use on marine oil spills and modern dispersants are orders of magnitude less toxic than the degreasers used on the *Torrey Canyon* spill.

Environment Canada has done extensive testing of dispersants and chemical cleaners (Fingas, et al, 1991, 1995) using standard tests with rainbow trout to assess the toxicity of more than 60 products. Common household detergents were included for comparative purposes and to help provide the proper perspective on dispersant toxicity. As stated previously, the greater the LC₅₀ or EC₅₀ value, the lower the toxicity. Table 9.2 shows that today's dispersants are an order of magnitude less toxic to rainbow trout than common household detergents are.

Table 9.2 Environment Canada Aquatic Toxicity Comparison of Household Cleaners and Dispersants (dispersants are in red)

PRODUCT	RAINBOW TROUT 96 HOUR LC ₅₀ (PPM)
Palmolive	13
Sunlight	13
Bioorganic	18
Mr. Clean	30
Citrikleen XPC	34
Enersperse 700	50
Lestoil	51
Corexit 9527	108
BP 1100 WD	120
Oil Spill Eater	135
Corexit 9500	354
BP 1100X AB	2900

9.3.1 Dispersant Concentrations in Marine Waters

There are few measured data for concentrations of dispersants in marine waters following an application during actual oil spill incidents, although in one case, a maximum concentration of 13 ppm was measured at a depth of 0.6 meters (Bocard, et al, 1984). However, average expected levels can be readily estimated from the dispersed oil concentration and the applied dispersant to oil (DOR) ratio. After its in-depth study, the National Research Council concluded that, at recommended application rates, the initial concentration of dispersant would be expected to be a maximum of 10 ppm and would rapidly decrease to less than 1 ppm within hours (NRC, 1989).

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Lewis and Aurand (1997) estimated a dispersant concentration of 5 ppm at a depth of one meter based on a standard application rate (dispersant-to-oil ratio of 1:20). They calculated that the 5 ppm concentration would be maintained only for a few minutes due to mixing and dilution. This is probably the high end of the range because dispersing a 0.1 mm thick oil slick (a common planning basis) into a 10 meter deep sea column results in an initial average **oil** concentration of 10 ppm. The initial average **dispersant** concentration would be 1/20th to 1/100th at this level (i.e., 0.5 to 0.1 ppm) and dilution would rapidly lower that concentration in the water column.

If the maximum initial concentration (10 ppm) of dispersant was sustained for 24 to 96 hours, early zooplankton life stages (eggs, larvae) and sensitive species such as crustaceans could be adversely affected by dispersant exposure in the upper layers of the water column. However, dilution and mixing rapidly reduce concentrations to less than observed laboratory effect levels in the first few meters of the water column. For many species, laboratory effect levels for dispersants are higher than 10 ppm. Also, organisms are typically exposed in laboratory tests to a **constant** dispersant concentration for up to 4 days. Based on these considerations, it is likely that **standard 2-4 day laboratory tests significantly overestimate adverse effects of dispersants in open water** (also see Figure 9.2).

9.3.2 Factors Affecting Dispersant Aquatic Toxicity

Though the primary determinants of toxicity to an organism are the concentration and duration of exposure, aquatic toxicity is also influenced by a range of other variables, including specific species sensitivity, life stage, and temperature. ExxonMobil's Anita George-Ares and Jim Clark summarized toxicity data for Corexit dispersants in 2000 (George-Ares and Clark, 2000) and later updated the information. See Appendix C for their summary of detailed toxicity data through 2003.

In this section, Tables 9.3 through 9.6 provide summary aquatic toxicity data for Corexit 9500 and Corexit 9527 dispersants. These tables demonstrate clearly the variability among species and test methods in toxicity levels associated with various dispersant products. Juvenile and adult fish are generally less sensitive (have higher LC₅₀ values) to Corexit 9500 than juvenile and adult crustaceans and mollusks. Similar trends are observed for Corexit 9527. Test data from around the world also indicate that early life stages of algae, mollusks, and fish are generally more sensitive to dispersants than adults of the same species.

As expected, decreasing the duration of exposure to a dispersant will reduce the potential for adverse effects. This is demonstrated by comparing the LC₅₀ or EC₅₀ values from the California test (spiked declining exposure) to values generated from 24- to 96-hour exposures (Tables 9.3 to 9.5).

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Table 9.3 Aquatic Toxicity Data for Corexit® 9500 (George-Ares and Clark, 2000)

SPECIES and LIFE STAGE	STANDARD STATIC TEST (24 TO 96 HOURS) LC₅₀ OR EC₅₀, ppm	CALIFORNIA TEST (2 TO 4 HOURS) LC₅₀ OR EC₅₀, ppm
Crustaceans Juvenile and adult Early life stages ¹	3.5 to 35.9 48	159 to 1038 -
Mollusks Juvenile and adult Early life stages ¹	42.3 -	- 12.8 to 19.7
Fish Juvenile and adult Early life stages ¹	50 to > 400 20- to 74.7	- > 1,055
Algae Adult Early Life stages ¹	20 0.7	- -

¹ Zoospores, embryos, larvae

Table 9.4 Aquatic Toxicity Data for Corexit® 9527 (George-Ares and Clark, 2000; App. C)

SPECIES and LIFESTAGE	STANDARD STATIC TEST (24 TO 96 HOURS) LC₅₀ OR EC₅₀, (ppm)	CALIFORNIA TEST (2 TO 4 HOURS) LC₅₀ OR EC₅₀, (ppm)
Crustaceans Juvenile and adult Early life stages ¹	3 to > 1,000 11.9 to 81.2	1,014 -
Mollusks Juvenile and adult Early life stages ¹	33.8 to 100 1.6 to 3.1	- 13.6 to 18.1
Fish Juvenile and adult Early life stages ¹	< 40 to 400 14.6 to > 100	- 58.3 to 104
Algae Adult Early life stages ¹	30 to 80 No data	- 86.6 to 102
Seagrass Juvenile and adult	200 (@ 96 hrs)	Not applicable
Giant Kelp Zoospores	1.3-2	12-102

¹ Zoospores, embryos, larvae

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Table 9.5 Comparison of “Standard” vs. “Spiked” LC₅₀s for Individual Species (George-Ares and Clark, 2000 and Appendix C) (all in ppm)

Dispersant and Species	48 hr LC ₅₀	96 hr LC ₅₀	Spiked LC ₅₀
C-9527			
• Gulf Mysid	24	19-34	>1000
• Kelp Forest Mysid	-	2-15	120-195
• Red Abalone Embryos	1-2	-	14-18
• Top Smelt Larvae	-	25-40	60-100
• Inland Silverside Larvae	-	15-57	58
• Giant Kelp Zoospores	1.3-2.1	-	12-102
C-9500			
• Gulf Mysid	32	30-36	330-1000
• Turbot	75	-	>1055
• Tanner Crab Larvae	-	24	1267
• Red Abalone Embryos	.7	-	6-20
• Inland Silverside	-	55	115

After reviewing all data regarding spiked and standard static test results, it can be concluded that **measurement by standard tests dramatically over-predicts actual toxicity by up to 35 times for dispersants** (dispersed oil is discussed in section 9.4). Figure 9.2 helps visualize how the spiked California test is a better simulator of the actual exposure following a dispersed oil bloom into the water column than the standard static test.

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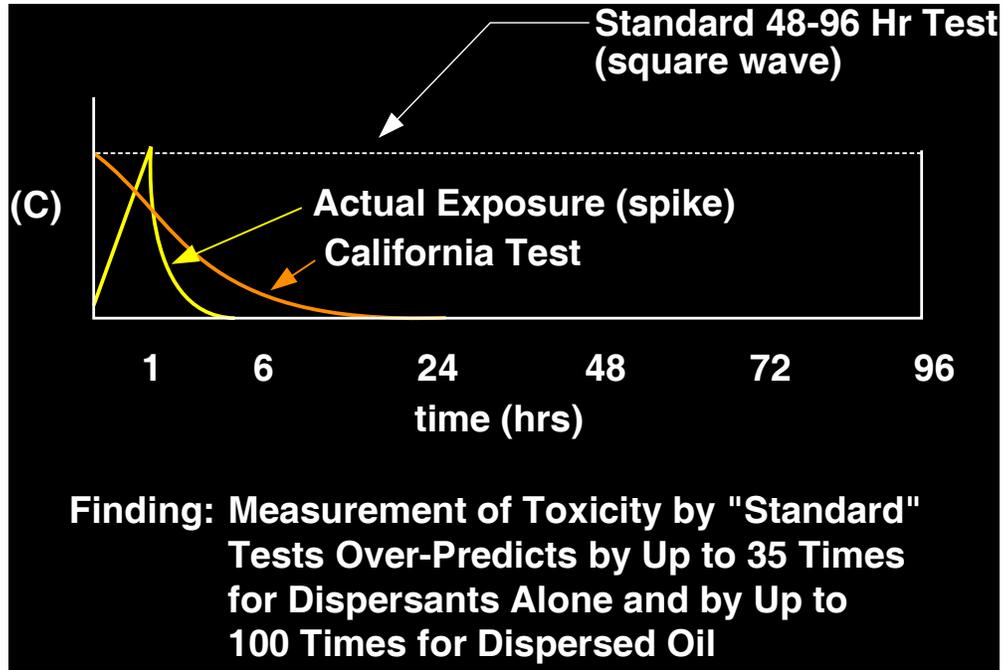


Figure 9.2 Simulated Profiles for Standard and California Tests vs. Actual Exposure

The chemical composition of a dispersant is another factor that affects aquatic toxicity. For example, Corexit 7664, a water-based product that is no longer manufactured, had a much lower toxicity (Table 9.6) to marine species than either Corexit 9527 or Corexit 9500, which are solvent based. The effectiveness of 7664 was found to be much lower than that of the other products.

Table 9.6 Aquatic Toxicity Data for Water-Based Corexit 7664 (NRC, 1989)

SPECIES	STANDARD STATIC TEST (48 TO 96 HOURS) LC ₅₀ ppm
Crustaceans	> 1,000 to 130,000
Mollusks	250 to 1,500
Fish	130 to 13,400
Worms	> 1,000

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9.3.3 Summary of Dispersant Aquatic Toxicity

According to the **US National Research Council (1989)**, “It is unlikely, based on concentrations of dispersants that would result from spraying in marine waters at common rates, that dispersants would contribute significantly to lethal or sub-lethal toxicities. Acute toxicity of chemically dispersed oil is generally similar to that of untreated oil in the water column.” That is, the dispersant does not add to the toxicity of the dispersed oil.

Modern commercially-available dispersants generally are of low toxicity. It is the ecological effects of the dispersed oil rather than the dispersant itself, that are of prime concern (Post *Braer* spill conclusion).

Basing product approval on dispersant toxicity alone is not appropriate. For example, in the US there is no requirement for dispersants to meet a toxicity limit for approval; toxicity data are collected for product comparison purposes only. However, in cases where dispersant toxicity testing continues to be required, then tests based on short-term spiked exposures should be employed because such dynamic tests are much more relevant to the marine environment than multi-day static tests.

9.4 Dispersed Oil Toxicity

The composition of crude oils and refined products is highly variable. Therefore, aquatic toxicity of oils also varies widely. The quantity of water-soluble components present in the oil has been the prevalent toxicity concern because aquatic organisms are exposed to the readily-water soluble components to a much greater and more intimate degree than to other types of oil molecules present in the petroleum material. The more highly-water soluble components of oil are predominantly mono-aromatic hydrocarbons and low molecular weight ($\leq C_{12}$) n-paraffins. Generally, the concentration of water-soluble molecules in crude oils is very low, much less than 1%. In addition, there are many opportunities for these to be extracted during the production and transportation life of crude oils due to contact with relatively large amounts of water. Moreover, these water soluble components tend to be the most volatile and/or degradable. In fact, a large percentage of the volatile components will evaporate within 5 to 12 hours of an oil spill (Betton, 1994; McAuliffe, 1989). As a result, evaporation makes up a major part of the weathering process. A benefit of weathering is that, as oil weathers, it tends to become less toxic.

More recently, oil toxicity research has focused on the polycyclic aromatic hydrocarbon (PAH) fraction of the oil as a toxicity concern. These molecules, although less water soluble than the monoaromatic constituents in the oil, have proven to be persistent in the environment and potent toxicants in the biochemical processes of exposed fish, crustaceans, and mollusks (NRC, 2003). While the PAHs make up a smaller percentage of crude oil components than the monoaromatics, their environmental persistence and potential for toxic impact have made them the focus of environmental toxicologists and they command significant attention in evaluating the potential impacts of oil spills and the use of dispersants to mitigate spill impacts.

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Some laboratory studies that addressed aquatic toxicity of dispersed and non-dispersed oils, were interpreted as indicating that dispersants add to the toxicity of the oil (NRC, 1989). However, dispersants move oil into the water column at a higher rate than oil that disperses naturally without the benefit of dispersants. The apparent greater toxicity of oil observed when it is combined with dispersant is due more to the increased exposure of aquatic organisms to dissolved and dispersed components of oil because of the higher availability in the water following the use of dispersants than it is to the presence of the dispersant itself. When toxicity estimates are made based solely on comparable fractions of petroleum components organisms are exposed to, there is no difference in aquatic toxicity between physically and chemically dispersed oil (NRC, 1989; Pace, et al, 1995).

Based on mesocosm experiments conducted during the 1980s the most significant effect following chemical dispersion is an immediate increase in the hydrocarbon exposure to plankton (NRC, 1989), particularly in the upper water layers where concentration is highest. The predominant toxicity mechanism is likely physical coating of organism surfaces (skin, gills, filterine appendages) by non-soluble oil components, though the soluble fraction also plays some role. Almost immediately, however, the dispersed oil is subject to rapid dilution and mixing by currents and wave energy. In open-ocean situations, dispersed oil would be diluted much more rapidly than in mesocosm tests (Lewis and Aurand, 1997). It is unlikely that an exposure concentration of 10 ppm dispersed oil will be exceeded in the open marine environment at depths below the top ten meters of the water column (SEA, 1995).

Clearly, the most sensitive species and life stages can be adversely affected even by short exposure to oil in the water column. Some sensitive life stages are susceptible to oil concentrations as low as 5 ppm, even on a spiked basis, so there can be localized impacts on these sensitive life forms. Table 9.7 summarizes “standard” and “California spiked” data for dispersed oil effects on sensitive life stages generated by ExxonMobil (Kuwait oil) and by the University of California, Santa Cruz and the University of Alaska, Fairbanks (ANS oil) as part of the CROSERF (Chemical Response to Oil Spills: Ecological Effects Research Forum) project. An entire session was devoted to CROSERF papers at the 2001 International Oil Spill Conference in Tampa, Florida. See pages 1231-1269 of the IOSC 2001 Proceedings for the seven papers presented. The impacts of naturally and chemically dispersed oil were found to be comparable. Because the oils used in these laboratory tests were fresh oils, i.e., unweathered, the results are most likely to be indicative of worst case effects. Additionally, the species used in the tests reported in Table 9.7 are among the most sensitive in nature. Natural mortality of these early life stages of marine species is characteristically high. To compensate, many planktonic species have short replacement times (days to weeks) and it is also possible that species recruitment can occur from adjacent waters not impacted by oil.

Long-term or significant impacts of dispersed oil to the general aquatic populations have not been reported as part of follow-up studies from oil spill incidents around the world. The comparable LC₅₀ levels for mature fish are orders of magnitude higher than the levels shown in Table 9.7. Recall that,

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in the UK toxicity test, 1000 ppm oil must be used in order to register toxic effect on mature brown shrimp. To our knowledge, there has never been a reported wild fish kill resulting from an oil spill. Unless they are confined in farms, fish have an innate ability to detect the presence of harmful oil and swim away (Weber, et al, 1981; Rice, 1973).

Table 9.7 Comparison of “Standard” and “Spiked” LC₅₀s for Dispersed Oil (PPM) on the Most Sensitive Life Stages of the Most Sensitive Species (from ExxonMobil, UC Santa Cruz, U of Alaska, 2001 IOSC)

Oil Type and Sensitive Species	48 hr LC ₅₀	96 hr LC ₅₀	Spiked LC ₅₀
Physically Dispersed Fresh ANS			
• Gulf Mysid	-	2.6	8.2
• Kelp Forest Mysid	-	-	14.2
• Topsmelt Larvae	-	-	12.1
• Tanner Crab Larvae	2.5	-	9.7
Chemically Dispersed Fresh ANS			
• Gulf Mysid	-	1.4	5
• Kelp Forest Mysid	-	<1.4	11
• Topsmelt Larvae	-	1.1	17.7
• Tanner Crab Larvae	1.3	-	10.7
Physically Dispersed Fresh Kuwait			
• Gulf Mysid	-	0.6	>3.0
• Inland Silverside Larvae	-	1.0	>1.3
• Oyster Larvae	>1.1	-	>1.8
Chemically Dispersed Fresh Kuwait			
• Gulf Mysid	-	0.6	17
• Inland Silverside Larvae	-	0.6	6.5
• Oyster Larvae	0.5	-	1.9

9.4.1 Dispersed Oil Toxicity Summary

“Acute biological effects are expected to be slight in most open-sea applications because the dispersed oil mixes into a relatively large volume of water, resulting in concentrations and times of exposure that are low compared to those showing effects in laboratory studies” (US NRC, 1989). As for PAHs referred to earlier, Dr. Merv Fingas has reported that PAH content correlates positively with dispersion (Fingas, 2007). The higher the PAH content, the higher the dispersion. Therefore, dispersants can be viewed as an effective tool for rapid dilution and dissemination of PAHs, which in many cases is likely to be of greater net environmental benefit than allowing undispersed PAHs to accumulate and persist in sediments and sensitive habitats.

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Conclusion: In assessing the overall net environmental benefit of a dispersant response, one must balance the positive effect of using dispersants to reduce oil impacts on sensitive wildlife and shoreline habitats, which recover slowly, against the dispersed oil causing a temporary loss of sensitive marine (primarily plankton) species that have exponentially greater replacement capabilities. Catastrophic losses of mature fish populations resulting from responsible dispersant applications have never been reported and are unlikely to occur because resulting concentration levels in the water column are well below most mature fish toxic thresholds.

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10.0 HUMAN HEALTH AND SAFETY

Today's generation of dispersants should not pose a health risk to spill response workers or the general public provided they are used with proper protective equipment, following sound operational procedures. Modern dispersants are formulated to be safer than the early products for use in the environment and are made of surfactants and solvents that pose little inherent danger to humans. Some countries require submission of chemical formulations upon registering and will prohibit products containing any ingredients with severe human health concern. Carcinogenicity is one of the screening factors used in the dispersant approval process of some countries. To our knowledge, none of the commercial dispersant products stored in the Tier 3 centers contain carcinogenic material. Biodegradability is also a factor often considered in gaining approval for use in a country as products that readily degrade are less likely to pose significant environmental or human risks compared to persistent products.

Some of the ingredients used in modern dispersants are found in many common household products, such as shampoos, cleaners, and carpet cleaners. Studies have shown that some household products can in fact be more harmful to aquatic species (see preceding chapter) than some commonly-used dispersants. Some of the common dispersant surfactants, e.g., "Span" and "Tween" (Sorbitan Oleates), are also used in the food industry.

Nevertheless, dispersant products formulated for industrial uses may have higher concentrations of surfactants and solvents than the household products and care should be taken to minimize contact with the skin and to minimize excessive inhalation of mists that may be generated. Workers whose jobs involve frequent and close contact with dispersants should wear the proper protective equipment and clothing, as specified on the manufacturers's Material Safety Data Sheets (MSDSs), used to alert users of potential risks. Workboat workers, for example, should not stand directly in the line of any dispersant spray from the application booms without appropriate face or skin protection. Figure 10.1 shows a Clean Caribbean and Americas worker who could be maximally exposed during a dispersant operation wearing proper protection while applying dispersants by boat.

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Figure 10.1 Proper Protection for Maximally Exposed Individual While Applying Dispersants by Boat

Potential effects from use of dispersants and recommended actions include:

- **Eye irritation.** Flush the eyes with water for 10-15 minutes after contamination.
- **Dermatitis.** Wash skin immediately after contact.
- **Nose and throat irritation.** Move to fresh air immediately.
- **Liver and kidney impact.** This has been reported as a possible effect from 2-butoxyethanol and is covered next.

10.1 2-butoxyethanol

Some dispersants contain 2-butoxyethanol (2-BE) solvent which can enter the body through the skin and by inhalation and can affect internal organs. There have been a few reports of such impacts and, in each case, there was clear indication that proper protective equipment was not being worn, leading to extreme exposure. Reported impacts include blood in the urine and temporary accumulation of 2-BE in the liver and kidneys. The literature on 2-BE and actual exposure studies indicate that the impact is short-term and begins to clear up within 24 hours following exposure (Johanson and Boman, 1991). Immediate washing of the skin is extremely prudent. There have been many reports of mild skin contact without adverse indications. 2-BE is fairly common in many industrial products and, when proper protective measures are applied, there is considerable experience showing that it can be safely handled without adverse effects.

Examples of handling guidelines that have been identified in MSDSs for 2-BE are:

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- Avoid skin contact when using products containing 2-BE. If contact occurs, wash with water immediately.
- Avoid spraying products containing 2-BE in a manner that will produce large amounts of overspray or vapor exposure to workers. Keep workers away from such areas to the extent possible.
- If workers must be in high-concentration areas, they should wear proper protective equipment:
 - Respirators (Monitor by charcoal tubes or badges)
 - 20-200 ppm - Half facepiece respirator with organic vapor cartridges
 - 200-2000 ppm - Full facepiece respirator with organic vapor cartridges
 - >2000 ppm - SCBA, Self-Contained Breathing Apparatus
 - Gloves and clothing
 - Use Butyl, Neoprene, Nitrile, Viton, or Saranex™
 - Wear chemical goggles
- Position workers upwind or sidewind.
- Decontaminate (wash) contaminated clothing before next use.

10.2 Other Precautions

In the *Braer* incident, dispersants and spilled oil were blown ashore by high winds and landed on sheep and vegetation. No harm to the sheep was reported and the vegetation suffered temporary setback from combined dispersant and oil exposures, but recovered completely by the following growing season.

The following are additional considerations in assessing whether to employ dispersants:

- Does the proposed area for spraying dispersants include the shoreline?
- Is there potential for high onshore winds if spraying is close to land?
- Are workers conducting response activities in the proposed spraying area?
- Is the proposed spray area a wildlife area?. The surfactants in dispersants could affect the insulating and buoyancy properties of bird feathers should they be sprayed.

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11.0 DISPERSANT USE NEAR SHORE

In most countries, dispersants are pre-approved for use with a proviso that they not be used in waters of less than a specified depth in order to ensure abundant water for dilution. The UK was the first country to impose a depth requirement of 20 meters for pre-approved dispersant areas and other countries have followed that example, but with varying depth limits. Table 11.1 presents some of the depth limits for dispersant pre-approval currently in place around the world.

Table 11.1 Depth Requirements for Dispersant Pre-Approval in Certain Countries

Country	Depth Requirement
Argentina	10 Meters
Bermuda	3 Meters
France	Down to 5 Meters (depending on spill size)
Malaysia	10 Meters
Nicaragua	No Limit
US (Gulf Coast)	10 Meters
UK	20 Meters

The country that permits use of dispersants right up to the shoreline more than any other is the UK, where depth restrictions for pre-approval were first imposed. The UK's 20 meter rule, as it is referred to, merely requires that responders contact the Department for Environment, Food and Rural Affairs (DEFRA, formerly MAFF) to gain authorization to spray dispersants in shallower water. Approval for near-shore use has often been granted in the UK and there is even an approval test for dispersants used on certain types of shorelines that all products must pass to be registered. As an example, responders to the 1996 *Sea Empress* spill in Wales, UK successfully used dispersants to clean stranded oil from areas adjacent to beaches without noticeable adverse effects (Lunel, et al, 1996).

Other countries should consider the adoption of the UK practice of approving use near- or on-shore, as spraying in these areas can often be quite advantageous in expediting spill response and result in a net benefit to the environment. Consideration of dispersant use in shallow waters near shore is gaining momentum in a number of countries, and has been the subject of an ongoing active dialogue in the US. Several of the pre-authorized areas around the US now have provisions to at least consider dispersant use in shallow waters during an emergency response and there are formal policies and procedures in place for such consideration in the Gulf of Mexico.

11.1 The Evidence Supports Dispersant Use Near Shore

Because of the high cost involved and the difficulty of obtaining permits for intentional releases of

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oil and dispersants, only a few well-planned tests have been carried out to assess the viability and safety of dispersing oil near- or on-shore. Three are reviewed here and a fourth is reviewed in the following section. They all conclude that dispersants can be safely applied to the near-shore environment with minimal environmental damage. In every case, dispersed oil impact was found to be no worse and often less than that of a comparable amount of untreated oil stranding on a shoreline. **The clear major benefit was the rapid removal of the dispersed oil from the area allowing habitat recovery to begin, compared to the prolonged presence of the untreated oil and its attendant lingering impacts.** The three tests summarized here include the **SERF** studies in Texas, coordinated by Texas A&M University; the **BIOS** study in Canada, conducted by Environment Canada; and the **API Searsport** study, carried out by professors and graduate students at Bowdoin College in Maine.

11.1.1 SERF (Aurand, et al, 1999; Bragin, et al, 1999; Page, et al, 1999)

In 1998, tests were conducted at SERF (Shoreline Environmental Research Facility) in order to evaluate dispersant use in a simulated near-shore environment. SERF is a group of nine test tanks located near Corpus Christi, Texas, constructed with MSRC funding in the 1990s and specifically designed to be hydrodynamically scaled for studies on oil spill impacts on near-shore habitats. In the 1998 tests, the near-shore environment was simulated in eight wave tanks, 33.5 m long, 2.1 m wide, and 2.4 m deep. Fresh seawater was circulated through the tanks to simulate tidal flow. A sandy inter-tidal zone was built at the end of each tank.

The fate and effects of both untreated and chemically-dispersed Arabian medium crude oil were compared. In three tanks, untreated weathered oil was allowed to strand in the inter-tidal zone. In three other tanks, weathered oil was dispersed with Corexit 9500, then the dispersed oil was allowed to enter the inter-tidal zone. The two remaining tanks served as controls to assess the impacts of physical conditions on the test organisms. Water and sediment samples were collected from the tanks for hydrocarbon analysis. Fiddler crabs were placed in cages in the upper inter-tidal zone (Figure 11.2). Snails (*Littorina*) were placed in cages in both the upper and lower inter-tidal zones. Eastern oysters were attached to substrates in the lower inter-tidal zone and in the water column. Caged polychaetes (worms) were placed in the sub-tidal zone. Sheepshead minnows and grass shrimp were used to evaluate water column exposures. In addition, sediment samples were collected from the tanks for laboratory toxicity tests on amphipods.

Despite initial dispersed oil concentrations near 50 ppm in the dispersed oil tanks, no significant toxic effects of any kind were observed on crabs, fish, oysters, shrimp, or "lower inter-tidal" snails exposed to either chemically dispersed or untreated oil. "Upper inter-tidal" snails showed sub-lethal effects (inability to right themselves within 5 minutes after being placed on their shells) following a 10 day exposure to both chemically dispersed and untreated oil. In this case, the dispersant did not add to the effects of the untreated oil alone. Data for the worms was inconclusive due to high mortality in control specimens.

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Figure 11.1 shows untreated oil coming ashore in one of the tanks. Figure 11.2 shows untreated oil on the sand 48 hours after test initiation; oil has stranded in the upper inter-tidal area. Figure 11.3 shows a dispersed oil tank 48 hours after test initiation; stranding of oil in the upper inter-tidal area in the dispersed oil tanks was much less than in the untreated oil tanks. A mass balance analysis at the end of the 10 day experiment showed that approximately half of the untreated oil remained sorbed to sediment and tank surfaces. By contrast, most of the chemically dispersed oil had flushed out of the three test tanks in 1 day.

In summary, the principal SERF results were:

- For all the water column species, there were no significant acute lethal effects observed in any of the tests, even though dispersed oil levels were initially 50 ppm, washing out over 24 hours (Bragin, et al, 1999).
- In the upper inter-tidal zone, amphipod tests showed a greater toxic response to untreated oil-impacted sediments than to dispersed oil-impacted sediments. In the sub-tidal sediment, amphipod mortality was higher in the chemically dispersed tanks. Overall, however, the lethal plus sub-lethal effects were the same for dispersed and untreated oil tanks (Fuller, et al, 1999).
- Beach contamination was extensive in the untreated tanks while there was no residual contamination in the untreated oil tanks (Page, et al, 1999).



Figure 11.1 Untreated Oil Stranding on SERF “Shoreline”

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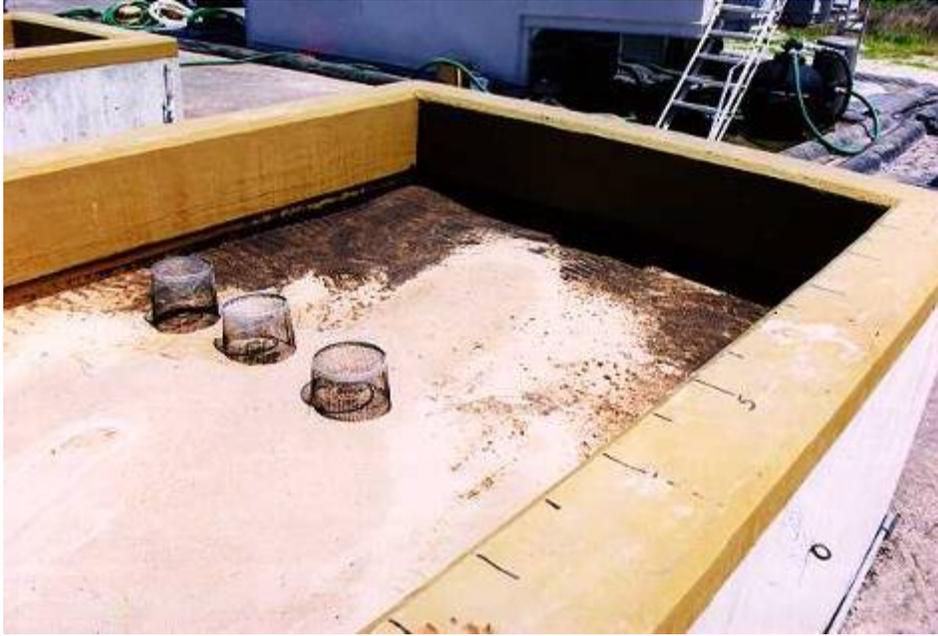


Figure 11.2 Stranded Untreated Crude Oil in the Upper Inter-Tidal Area After Approximately 48 Hours



Figure 11.3 Stranded Dispersed Oil in the Upper Inter-Tidal Area After Approximately 48 Hours

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11.1.2 BIOS Project (Blackall and Sergy, 1983; Cutter Information Corp., 1986)

From 1980 to 1983, Environment Canada and the Canadian Petroleum Association co-sponsored a test program called the Baffin Island Oil Spill or BIOS Project. In this cold water project (-1.7 to 4.5° C), untreated crude oil and chemically dispersed oil were released off Baffin Island in Canada. The objective was to assess whether near-shore use of chemical dispersants on oil slicks in the Arctic would reduce or increase the biological impacts of spilled oil. Corexit 9527 was used to disperse the crude oil. Cape Hatt on northern Baffin Island was chosen as the test site because its shorelines and near-shore environments are representative of the arctic and sub-arctic coasts. The area is iced-in except during July and August. Hydrocarbon concentrations were monitored in water, sediment, and aquatic animal tissue.

The BIOS Project conclusions were:

- There are no major ecological reasons to prohibit the use of chemical dispersants on spilled oil in near-shore areas similar to the Baffin Island site.
- Use of chemical dispersants in coastal areas can be an environmentally acceptable response and can reduce the net negative effect of spilled oil (*i.e., it can offer a net environmental benefit*).
- Dispersant use may be the only choice when the protection of shoreline and near-shore habitats has priority and where shoreline cleanup is environmentally less desirable.

According to Environment Canada's Sergy: "Effective near-shore chemical dispersion will be preferable in many situations where shoreline protection is of prime importance or where it is desirable to reduce the duration of exposure of sub-tidal benthos to oil. Likewise, it will most often be the preferred alternative to intensive shoreline cleanup" (Sergy, 1985).

11.1.3 API Test, Searsport, Maine (Gilfillan, et al, 1983)

In August 1981, an API-sponsored field experiment was conducted by Bowdoin College at Long Cove, in Searsport, Maine. The experiment was designed to evaluate the efficacy of dispersing oil slicks near shore in areas of extreme tides (over 5 meters). The objective was to obtain data on the fate and effects of both dispersed and non-dispersed oil in the near-shore area. In the dispersed oil test, 250 gallons of Murban crude oil pre-mixed with 25 gallons of Corexit 9527 was released at high-water slack tide. Unfortunately, logistical constraints prevented the running of all tests on the same tide. In the untreated test, 250 gallons of Murban with no dispersant was released during an ebbing tide.

Two 60 x 100 meter test plots containing upper and lower inter-tidal areas, were exposed to either untreated oil (Figure 11.4, plot I), or dispersed oil in water (Figure 11.4, plot III). A third plot served as an un-oiled control (Figure 11.4, plot II). The maximum water depth was 3.5 meters.

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Despite the inability to run all tests on the same tide, the results are thought to be generally indicative of what would happen under actual spill conditions even if the tests were imperfect.

Dispersed oil concentrations ranging from 15 to 20 ppm were measured in the water 10 cm from the bottom. After just one tide change, no measurable amount of oil remained in the sediments exposed to dispersed oil. All of the dispersed oil had been removed through tidal action. The untreated oil, however, remained on the shoreline and exerted effects on marine life for several months.

Concurrent chemical and biological analyses were made during pre- and post-spill periods in order to evaluate the effects on the inter-tidal infaunal community structure. Infauna refers to animals that live within sediment. A total of 21 infaunal species (crustaceans, mollusks, and worms) was studied.

The main results of the Searsport test were:

- There were no detectable adverse effects on infaunal community structure from exposure to dispersed oil.
- There was significant incorporation of oil into sediments exposed to untreated oil, with more being found in the upper shore than the lower.
- Untreated oil caused high oil intake and mortality in a commercially important clam and increased densities of opportunistic polychaete worms in the inter-tidal zone.
- Effects on biological community structure resulting from exposure to untreated oil were long-term and consistent with findings from actual oil spills, indicating that the Searsport test was a realistic simulation.

Figure 11.5 is a photo of the shoreline exposed to the dispersed oil four hours after the release. There was no visible evidence of oil. Figure 11.6 shows the area where untreated oil went ashore. Untreated oil did not wash out and remained on the shoreline for considerable time despite high-energy tidal action.

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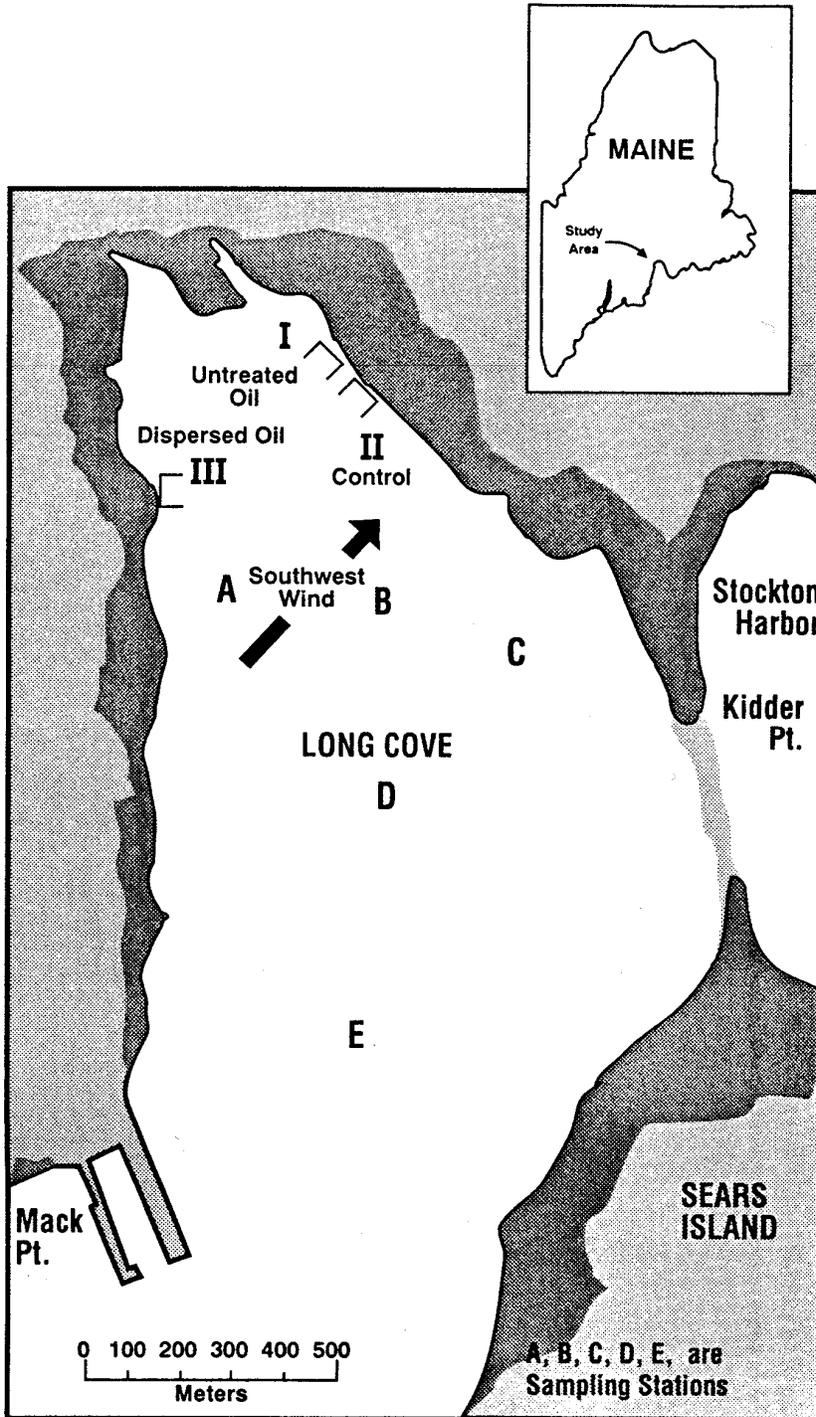


Figure 11.4 Map of Long Cove, Maine Showing Location of Test Plots I, II, and III

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Figure 11.5 Dispersed Oil Test Site Shows No Oiling Just Four Hours After Application

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Figure 11.6 Stranded Untreated Oil in Searsport Test

11.2 Conclusion Regarding Near-Shore Use of Dispersants

Based on the available data, oil can be effectively dispersed into near-shore waters with beneficial environmental results, provided there is good dilution and mixing potential. The clear benefit is the ability to quickly flush the oil out of the locality, minimizing the time of contact with infauna and accelerating the restoration of the environment to its pre-oiled condition.

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12.0 DISPERSANT USE IN THE TROPICAL REGION

The region referred to as the Tropics comprises the area that ranges from 23½ degrees north to 23½ degrees south of the equator. The Tropical Region is characterized by higher temperatures, abundance of sensitive habitats, very weak tides, and year-round tourist resorts. Dispersant response in the Tropical Region must take into account important local environmental and amenity features that can influence dispersant decisions. There have been some conflicts in deciding relative priorities of sensitive habitats such as between mangrove forests and amenity tourist beaches. Such conflicts regarding protection priorities may be difficult to resolve during a spill emergency and consideration should be given to sorting these out in advance by establishing the overall priority of resources for protection during pre-spill contingency planning. All of the resources are important to some part of the community and establishing a consensus regarding the relative priorities can be very complicated and contentious.

12.1 Effects of Higher Temperature on Oil

High temperature can both help and hinder dispersant response through the following effects on oil:

- Oil viscosity is significantly lower at high temperature. This can make even heavy oils more amenable to dispersion.
- Oils with high pour points are not as great a concern in the tropics as in colder regions.
- Weathering is significantly faster at high temperature because of higher evaporation rates. The overall effect of weathering is trending oil properties toward less effective dispersion, which may be offset to some extent by the lower viscosity of oils at warmer temperatures.
- Various fate processes such as spreading, emulsification, and tar ball formation are faster at high temperature. Depending on the oil, this could make dispersant response (and overall oil spill response) more urgent than at lower temperature.
- Biodegradation of oil (physically and chemically dispersed) is significantly enhanced at higher temperature.

12.2 Sensitive Habitats

A habitat is sensitive in the context of an oil spill if it has any of the following characteristics:

- Exposure to oil could result in significant biological impact on resident species.
- Oil impact could threaten the integrity and survivability of the habitat.
- Recovery (defined as return to pre-spill range of population abundance and diversity) following oil impact is long-term (years to decades).
- Oil could harm endangered, threatened, or protected species, e.g., migratory waterfowl and marine turtles.
- Oil impact could devastate the local economy. Examples are subsistence fisheries, tourist coral reefs and snorkelling areas, hotel beaches, fish farms, marinas, etc.

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In that context, the following habitat types are generally acknowledged as sensitive to oil spill impacts. They are presented along with recommendations for the preferred dispersant strategy for protecting them. In most cases, application of dispersants to oil in the immediate vicinity of sensitive habitats is discouraged, as the potential for maximum exposure concentrations could place the habitat at risk. If oil is clearly headed for a sensitive habitat, it should be dispersed at distances as far from the habitat as possible, requiring prompt decision-making as a crucial aspect of the survival of the sensitive areas.

12.2.1 Mangroves

Mangroves are important nursery areas that provide food and shelter for aquatic and terrestrial species. It has been estimated that up to two-thirds of the world's fish populations depend on detritus, nutrients, and the nursery protection of mangrove areas. In some parts of the world, mangrove habitats are of commercial and subsistence importance. In addition, mangrove forests stabilize the shorelines and their loss can result in serious erosion with deleterious impacts on local and adjacent habitats.

Oil can injure or kill mangroves through physical coating of the prop roots used by the trees for gas exchange (Figure 12.1).



Figure 12.1. Red Mangrove Prop Roots Are Vulnerable to Oil (ExxonMobil Photo Archives)

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Oil can also impact mangroves through the toxicity of lower molecular weight aromatics which damage cell membranes, but this is of lesser concern than the physical mechanism (IPIECA, 1993). Every effort should be made to keep oil from entering mangrove areas. If oil threatens to invade the area, dispersant use is a preferred response for protecting mangroves. Spraying should be done as far offshore as possible but, even if spraying is close to shore and dispersed oil is likely to enter the mangrove forest, this is preferable to untreated oil reaching the mangroves. Untreated oil can have a profound effect on a mangrove forest but oil treated with dispersant is less likely to adhere to mangrove prop roots, lessening the potential impact. Dispersants should be sprayed prior to the rising tide, if possible. If large amounts of dispersed oil enter a mangrove area and there is only limited tidal exchange, the dispersed oil should be flushed out using low pressure spray equipment from small boats to the extent possible without causing habitat harm.

12.2.2 Coral Reefs

Coral reefs (Figure 12.2) provide food, spawning/nursery grounds, and shelter for marine species. Coral reefs stabilize shorelines by dampening wave energy and provide sand to replenish beaches. In many areas, coral reefs are also important for recreation and tourism.



Figure 12.2 Coral Reef in the Red Sea (Courtesy, Anita George-Ares)

Dispersant use should be considered as a response method for protecting coral reefs. The emphasis should be on preventing floating oil from reaching the reef area by dispersing well offshore. For reefs that are exposed to air at low tide, oil should be dispersed as far from the reefs as possible in order to minimize potential stranding of oil (treated or untreated). Application of

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dispersant directly over shallow, submerged reefs is generally not recommended since coral and other reef organisms can be adversely affected by the initial high concentrations of dispersed oil. However, responders should weigh any potential adverse effects of high exposure to dispersed oil plumes against those effects that may occur if untreated oil enters other sensitive shoreline habitats. Coral reefs often occur near mangroves and seagrass beds. In such a case, the net environmental benefit of dispersant use requires careful consideration and difficult prioritization decisions will be required.

12.2.3 Kelp Beds

Kelp beds (Figure 12.3) typically occur near coastal areas, providing food and habitat for a diversity of marine species and are highly productive and valued habitats. Dispersant use is a viable technique for protection of kelp beds and their associated diverse communities, which occur most often in rocky sub-tidal habitats.



Figure 12.3 Kelp Bed (ExxonMobil Photo Archives)

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Dispersants should be used primarily in the protection mode well offshore and away from the kelp habitat. Aerial application near kelp beds is preferred over vessel application, as it allows more rapid and surgical application techniques and lower risk to the kelp. Dispersants should be used only where there is sufficient water circulation and flushing for dilution of dispersed oil. If spilled oil is floating above the kelp fronds and does not threaten a more important resource, oil should be left on the surface and allowed to move to other less sensitive open water areas, rather than being dispersed into the kelp. Dispersing oil directly over the beds is not advised unless doing so protects a higher priority species or habitat.

12.2.4 Sea Grass Beds

Sea grass beds (Figure 12.4) are important nursery areas and provide food and shelter for numerous marine species. By dampening waves and currents, sea grass beds play an important role in stabilizing sediments and shorelines.

Dispersant use well offshore to protect sea grass beds is viable and recommended. If floating oil occurs over a sea grass bed, the depth and dilution potential of the area should be considered in dispersant use decisions. Dispersant use in shallow areas or in areas with limited water exchange is generally not recommended as dispersed oil may affect organisms living in the sea grass bed. As with the other sensitive habitats, potential impacts of dispersing over shallow sea grass beds should be weighed against alternative impacts if oil comes ashore.



Figure 12.4 Sea Grass Beds (Courtesy, Florida Keys NMS)

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12.2.5 Salt Marshes

Salt marshes are very productive sources of food and shelter for both aquatic and terrestrial species. They are characterized by very low wave energy and high sedimentation rate. Oil entering salt marshes could remain for years and cleanup is rarely advised because of the possible damage to the substrate due to the intrusive nature of manual clean-up efforts.

Dispersant use is a viable response for open water and channel areas in the marsh, but not to the marsh surface itself. Without sufficient dilution, exposure of marsh communities to dispersed oil provides minimal environmental benefits. The dispersant should be applied on an incoming tide to maximize dispersion and washout. Caution should be used in non-surgical aerial application methods for dispersant treatments to prevent contamination of adjacent areas. Dispersants should not be used in marshes that have limited water exchange.

12.2.6 Tidal Flats

Tidal flats (Figure 12.5) are inter-tidal areas that are usually sheltered from waves. Mangroves, marsh grasses, or sea grasses may occur in tidal flats. Tidal flats provide nursery areas for large populations of animals and plants. In addition, these areas are important feeding and resting grounds for birds and other species. They have very low wave and flushing action and oil that enters these habitats can persist for long periods.

Offshore application of dispersants to protect tidal flats is preferred. Oil should be dispersed as far from shore as possible. If possible, dispersants should be sprayed prior to an advancing tide, as dispersed oil is less likely to adhere to sediment surfaces compared to untreated oil. Dispersants should generally not be applied to oil already stranded on a tidal flat.



Figure 12.5 Tidal Flats

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12.3 TROPICS Experiment

Deciding whether or not to apply dispersants based on net environmental benefit analysis (NEBA) is probably most problematic in a tropical region because of the prevalence of many different and sensitive habitats throughout the eco-system. In temperate areas, dispersing oil into the open sea to protect a salt marsh is straightforward. However, it is not so clear in Australia at the Great Barrier Reef where so much of the environmental value depends on tourism focused on the magnificent coral reefs that extend for over 1500 miles offshore. How does one weigh the impact on the reefs, if oil is dispersed into them, against the loss of a mangrove forest or other nearshore habitat, if oil is not dispersed?

Scientists sought to gather field data to help deal with this dilemma over two decades ago in a study sponsored by the Smithsonian Institute. The 1984 TROPICS experiment was carried out in Panama in an embayment containing mangroves on the shoreline and coral and sea grasses in the water, an aggregation of sensitive resources commonly found in tropical regions in Central America, Africa, Asia, and Australia. At one site, a total of 100 gallons of untreated North Slope crude was released slightly offshore and allowed to strand in the inter-tidal zone in proximity to mangroves, corals, and sea grass beds. At another site, a total of 100 gallons of North Slope crude oil premixed with Corexit 9527 dispersant was also released, again with these three sensitive habitats in the immediate area. A third site with all three habitats present was used as a reference untreated area (Getter and Ballou, 1985; Ballou et al, 1989).

The TROPICS field test conditions are viewed as an extreme or worst case scenario (IPIECA, 2001) because the average water depth was less than 1 meter and concentrations of dispersed oil in the shallow water reached over 200 ppm (see Figure 12.6). The TROPICS site has been intensely monitored during the past 20 years, with 18 separate studies conducted and reported over that period. The results serve as an excellent source of guidance information for responders to spills in comparable environments, providing clear evidence of the net environmental benefit of nearshore use of dispersants in tropical ecosystems (Baca, et al, 2005).

As in the near-shore field studies discussed in the preceding section, the dispersed oil site experienced less stranding of dispersed oil on sediment and nearshore surfaces and rapid removal of dispersed oil by tidal flushing. However, oil was not removed as promptly from the untreated oil site and still remains today. The results were:

- The untreated oil had significant effects on the mangroves. Even after 10 years (Dodge, et al, 1995 reported by Lewis and Aurand, 1997), the area still contained only half the original concentration of mangrove trees.
- There was no observed direct mortality on mangroves in the areas impacted by the dispersed oil. This is probably because dispersant kept oil from attaching to the sediments and mangrove prop roots and the dispersed oil flushed out rapidly.
- Corals were significantly affected by dispersed oil but not by untreated oil. But at the 10 year mark, those that had been impacted had recovered and no significant difference

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existed between experimental and control sites (Dodge, et al, 1995; Lewis and Aurand, 1997).

- Sea grasses were not affected by either treatment but invertebrates around the grasses were severely affected by dispersed oil.



Figure 12.6 Exposure of Mangroves to Oil in TROPICS Experiment

Scientists who continue to monitor the TROPICS site indicate that some of the original untreated North Slope oil is still present and occasionally seeps out, causing a low level of ongoing chronic impact in the area (Baca, et al, 2005). One conclusion from the Panama field test is that **adding dispersant to the oil going into a sensitive habitat and seeing it promptly flushed from the area is preferable to having untreated oil remain in a low-energy area with the potential for ongoing impact.** As one of the recent principal investigators, Dr. Bart Baca of CSA South, Inc. has said on many occasions, **protection of the habitat is more important for the ecosystem in the long term than any resulting shorter-term effects on organisms themselves.** Organisms can re-populate quickly as long as the habitat is preserved.

13.0 DISPERSANT USE IN COLD REGIONS

Based on the available literature, dispersant response is feasible in a cold environment, but is likely to be a greater logistical challenge than in temperate and tropical regions because of the unique challenges of working at low temperatures. Except for water-based products, most of the common dispersants should flow well through pumps and spray booms even at sub-freezing temperatures. In cases where problems have been encountered in the past, the problems have been traced to the freezing of residual water inadvertently left inside application equipment. Ensuring that spray booms, feed lines, and pumps are totally dried after use is a must in cold regions. This is especially relevant to systems that apply dispersants using a water carrier.

13.1 Effects of Low Temperature on Oil

Low temperature can affect oil in the following ways:

- Oils with relatively high pour points are more susceptible to solidifying.
- Oil viscosity increases significantly as temperature drops. The viscosity of fresh Kuwait oil, for example, nearly triples as temperature drops from 20°C to 0°C. The higher the oil's viscosity at 20°C, the greater will be its relative increase as temperature drops. A medium fuel oil's viscosity of about 2000 cSt at 20°C will rise to over 13,000 cSt at 0°C.
- More viscous oil spreads slower so slicks remain cohesive for a longer period of time.
- Loss of light ends by weathering slows down significantly. For example, the evaporation rate at 5°C is approximately 1/3 that observed at 30°C. Depending on the magnitude, retention of the light ends could offset a significant percentage of the viscosity increase due to low temperature.
- Emulsification and tar ball formation rates become slower as they also depend on weathering.
- Oil's biodegradation rate is less at lower temperature.

13.2 Dispersant Effectiveness at Low Temperature

There is considerable laboratory, wave basin, and field data demonstrating that dispersants are effective in cold water, even at 0°C. The BIOS project mentioned in section 11 demonstrated successful dispersant application in a cold region that is iced over 10 months of the year. During the past 30 years, some 2 dozen papers (see Appendix D) have been presented at the annual Arctic and Marine Oilspill Program Technical Seminar (AMOP), hosted by Environment Canada, that discussed the feasibility of dispersant application at low temperature. The earliest studies were conducted by Mackay and Wells (1981), Cox and Schultz (1981), and Byford (1982). Mackay and Wells actually suggested that in some exceptional cases dispersant effectiveness might be greater at low temperature, aided by ice turbulence. Cox and Schultz concluded emphatically that it is possible for dispersants to be effective in an arctic environment, and BP's D. C. Byford found that many commercial formulations and experimental blends worked satisfactorily at 0°C in the Labofina lab test.

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The *Braer* tanker spill in the Shetland Islands of Scotland and the *Sea Empress* tanker spill in Wales in the UK, during which significant quantities of oil were dispersed, occurred in the winter months of January and February, respectively. Testing carried out during the *Exxon Valdez* response in Prince William Sound, Alaska, showed that dispersants worked well enough at 4°C that the US Coast Guard gave full approval for dispersant use on the spill, though that approval came too late to be of significant help due to severe weather.

Wave Basin tests at the Esso Resources facility in Canada and at OHMSETT in the US have shown successful dispersion of oil even in the presence of broken ice. Brown and Goodman, 1996, found 90% or better dispersion by Corexit 9527 and Corexit 9500 even when 95% of the surface was covered with ice floes. Additionally, oil spilled among slush ice rapidly dispersed in their wave basin tests when treated with dispersant. Figure 13.1 is a photo of the Esso tests showing oil being dispersed in broken ice.



Figure 13.1 Oil Dispersing in Broken Ice (tan areas) During Canadian Tests (Brown and Goodman, 1996)

In 1991, Professor Don Mackay of the University of Toronto, a widely respected dispersant scientist, undertook a study on behalf of ExxonMobil at the Esso Resources Canada, LTD. wave basin to simulate conditions that existed in Prince William Sound, Alaska, following the *Exxon Valdez* spill in 1989. The objective was to determine how effective dispersants might have been

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had they been allowed to be used in a timely manner on the *Valdez* spill. The test oil was weathered Alaska North Slope crude. The dispersant was Corexit 9527, the product most widely stocked in Alaska at the time of the spill. Conditions in the basin were as close to those in Prince William Sound (PWS) as could physically be reproduced, i.e., salinity, temperature (4°C), wind speed, varying sea conditions, 1.3 mm thick oil film, etc. An in-depth laboratory test was run in parallel to verify and re-inforce the wave basin findings.

In the basin tests, the oil was allowed to stand on the water for up to 30 hours following dispersant spraying before initiating breaking waves. This was to simulate the calm conditions existing after the *Valdez* spill up until a violent storm arose some 30 hours after the hypothetical spraying might have been feasible. A simulated reef was added to induce breaking waves as a means of simulating the storm that arose at PWS. Following months of testing, Professor Mackay concluded that “the most significant finding is that, for the turbulent conditions in the wave basin, effectiveness values in the range of 90 to 100% were obtained at DORs (Dispersant to Oil Ratio) of 1:100. Even at 1:200 (up to 95% effective) and 1:300 (50% effective) significant quantities of oil were dispersed” (Mackay, 1995). The degree of dispersion achieved varied inversely with the length of time the dispersant remained on the oil. Best results were achieved when dispersant was applied immediately before the simulated storm. Not only was dispersion effective at low temperature in these tests, it was effective at extremely low dispersant concentrations because of the high energy.

A number of subsequent cold water dispersant tests have been carried out more recently at the Ohmsett wave basin in New Jersey, further verifying low temperature effectiveness. In 2002, a joint US government/industry program, funded primarily by MMS, was carried out specifically to address public concerns that dispersants might not be effective in Alaska’s cold waters. Using supplementary refrigeration to keep the water near freezing temperature, the Ohmsett operators, aided by S. L. Ross scientists who planned and coordinated the tests, showed conclusively that dispersants can readily disperse both Alaska North Slope and Hibernia (from Newfoundland, Canada) crude oils at -0.5 to 2.4°C (Belore, 2003). Table 13.1 summarizes the test results.

Table 13.1 Ohmsett Cold Water Dispersion Efficiency Results*

Dispersant	Fresh Oil Effectiveness	10% Weathered Effectiveness	20% Weathered Effectiveness
Corexit 9527 • ANS	>90%	>90%	85-95%
Corexit 9500 • ANS • Hibernia	>90% >90%	>90% 85-95%	85-95%

* Tested at 0°C, 30,000 ppm salinity, 0.5-0.75m wave height, no breaking waves

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These tests were witnessed and verified by experts and scientists from across government and industry. Efficiency was determined by collecting and measuring residual surface oil at the conclusion of each test. MMS subsequently carried out additional cold-water tests with ANS and crude oils from specific North Slope fields with similar results. Additional tests carried out with ice present re-affirmed earlier Esso wave basin and other studies that showed oil to be dispersible even in the presence of broken ice floes.

In summary, available data indicate that dispersants can be effective in even the coldest waters (even below 0°C) and should not be ruled out based on low temperature considerations alone.

14.0 DISPERSANT TYPES AND APPLICATION RATES

Dispersants vary in capability depending on the strength and concentration of surfactants and the type of carrier solvent used. For the dispersant to be effective, the surfactant blend must significantly lower the interfacial tension between the oil slick and water phase, thus significantly reducing both the amount of energy needed to disperse the oil and the size of the oil droplets that are produced. As discussed in section 6, effective dispersants must generate oil droplets that are small enough that their rise velocity is slower than the rate of turbulent mixing in the water column, allowing the dispersed oil droplets to remain suspended in the water column. The solvent carrier fluid has two very important functions: 1) reduce the viscosity of the surfactant blend to allow efficient dispersant application, and 2) promote penetration and mixing of the surfactant blend into the oil slick. The effectiveness of a particular dispersant depends on its composition and the state of the oil to be dispersed. Generally, modern commercial dispersants are relatively effective on fresh, low viscosity oils. As the oil weathers and loses light ends, the oil viscosity rises and the dispersant capability may decrease, depending on its makeup and relative strength.

14.1 Types of Dispersants

Dispersants are generally of three types, classed according to the solvents used in formulation:

- **water-based dispersants** - These are totally compatible with water. They always contain water and may also include light alcohols. The solvent in Corexit 7664, ExxonMobil's first dispersant product, comprised a blend of water and isopropyl alcohol. They are generally low in toxicity but are among the less effective formulations. They are ineffective on viscous oil and would probably not be suitable for use in cold climates where freezing temperatures could interfere with storage, transport and application.
- **conventional hydrocarbon-based dispersants** – These contain very low concentrations of surface active agents and are primarily used at high dispersant-to-oil ratios (DOR) in undiluted form. A solvent commonly used is de-aromatized kerosene. To be effective, as much as 1 part dispersant to 2 parts oil must be applied. Diluting such products with water is not recommended as it can reduce effectiveness. Because of the high DOR required, application operations are less efficient requiring frequent dispersant re-supply.
- **concentrate products** – These typically have higher surfactant concentrations, 40-60%, and mostly use hydroxy-compound solvents, such as glycol ethers, though some also use hydrocarbon solvents. Hydroxy-based products can be used either in neat undiluted form applied from aircraft or boat, or diluted with sea water and applied by boat spray booms.

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In the UK, dispersants are classified by Type according to the way they are tested and applied. Type 1 refers to **conventional** hydrocarbon-based dispersants above. Type 2 dispersants are **concentrate** products that are applied in a diluted water spray. Type 3 dispersants are **concentrate** products applied neat (undiluted). Some modern dispersants are registered as both Type 2 and 3 and can be used diluted or undiluted depending on the specific application system.

Table 14.1 summarizes the three types of chemical dispersants and indicates which oil type each is best suited for.

Table 14.1 Chemical Dispersant Types and Uses

Oil type	DISPERSANT TYPE		
	Water-Based	Conventional	Concentrate
Light Distillate Fuels ⁽¹⁾	✓		✓
High Spreading Rate Products and Crudes	✓	✓	✓
Low Spreading Rate Viscous Crudes, Heavy Oils, Weathered Oils and Emulsions			✓
Waxy Crudes with High Pour Point		✓ ⁽²⁾	✓ ⁽²⁾
Non-Spreading Oils (Solid)	Dispersion not feasible		
<p>Notes:</p> <p>(1) Dispersion suggested only in cases of fire hazard. High evaporation rate and toxicity of the oil reduces desirability of dispersion in other cases.</p> <p>(2) Dispersants are probably not effective if the water temperature is 10 °F below the pour point of the oil.</p>			

Table 14.2 summarizes dispersant types according to their compatibility with dispersant application methods by vessels or aircraft. For example, consider a dispersant concentrate. A dispersant concentrate is typically one having greater than 40% of surface active agents by volume and is, therefore, generally capable of dispersing a large volume of oil per volume of dispersant. If a concentrate is to be applied by a boat spray system, it frequently is applied in a

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seawater carrier system to achieve target application rates of 5-10 gallons per acre. Neat application by boat can achieve 20 gallons per acre or higher but may require modification of the equipment (pump rate, nozzles, etc) to achieve the proper dosage and distribution. Dispersant concentrates applied by workboats should be effective both when applied neat or in a seawater carrier system. If aerial application is to be utilized, the dispersant should be a concentrate applied neat to allow optimum use of the aircraft. Use of aircraft to apply dispersant that has been diluted with water generally is not advised.

Table 14.2 Chemical Dispersant Types Versus Application Methods

Application Method	DISPERSANT TYPES		
	Water-Based	Conventional	Concentrate
VESSELS Spray Booms Fire Systems	Dilute or Neat Dilute	Neat Not Recommended	Dilute or Neat Dilute
AIRCRAFT Helicopters ⁽¹⁾ Small Airplanes ⁽¹⁾ Large Airplanes ⁽²⁾	Not Recommended Not Recommended Not Recommended	Neat Neat Neat	Neat Neat Neat

⁽¹⁾ Not recommended if dispersant viscosity is less than 30 centiStokes (cSt), see Table 15.2.
⁽²⁾ Not recommended if dispersant viscosity is less than 60 cSt, see Table 15.2.

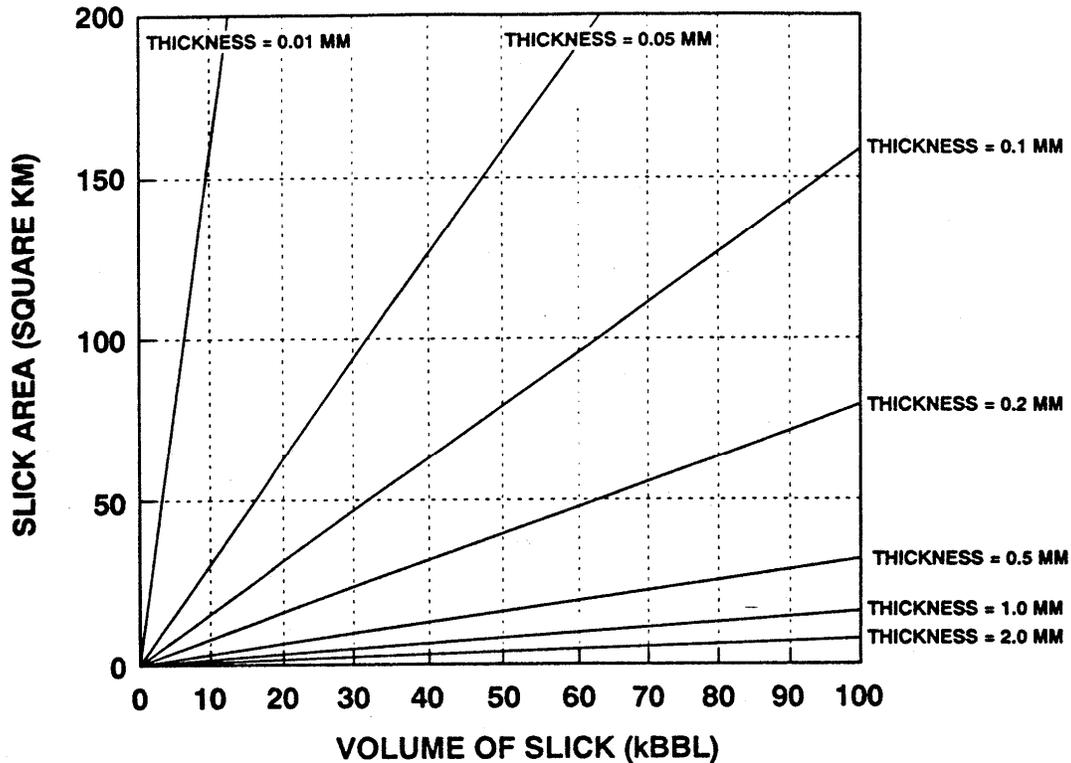
14.2 Application Rates

The dispersant-to oil ratio (dispersant:oil or DOR) is the volumetric ratio of the dispersant being used to the oil being treated. The conventional planning basis for dispersant dosage is 1 part dispersant to 20 parts of oil. Over the past 40 years, this ratio has proven to be a safe basis on which to plan dispersant operations, usually resulting in high effectiveness and very small dispersed oil droplets. However, this does not take into account the wide range of properties found in both oils and dispersants. For strategic planning purposes, weaker, lower cost dispersants are best used on light and relatively unweathered oils that are very amenable to dispersion, applied at a dose rate of 1 part dispersant to 20-30 parts of oil. For the same oils, however, more potent dispersants could be effective at lower dosage, even at 1 part dispersant to 100 parts of oil as Mackay found (Mackay, 1995). This is particularly true if the sea energy is quite high (e.g., characterized by breaking waves). For oils with average dispersibility, robust products could be applied at 1 part dispersant to 50 parts of oil, or more. For heavy oils or highly weathered or emulsified oils, products that have been shown to be effective on such oils (e.g., Corexit 9500 and Superdispersant 25) should be applied at a maximum of 1 part dispersant to 20 parts oil.

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With lighter oils, dispersion can occur immediately or very soon after application. For heavier or more weathered oils, dispersion may be delayed for some time as the surfactants diffuse to the oil/water interface more slowly, possibly taking up to an hour or more. In the case of heavy viscous oils, monitoring may therefore be required over a long period to confirm effectiveness. There have been many instances of initially reporting ineffective application (e.g., at the *Sea Empress* spill) only because those monitoring expected to see nearly instantaneous results and, in fact, dispersion was delayed for some time. In the end, the dispersant response to the *Sea Empress* spill was characterized as a major success.

Figures 14.1 and 14.2 are useful for estimating dispersant application dosage rate (Exxon Mobil Corp., 1985). Figure 14.1 is used as the first step, which is to determine the average slick thickness based on the slick area and known volume of oil spilled. For example, if the volume of oil spilled is estimated to be 60,000 barrels (bbl) and the slick area is estimated to be about 95 square kilometers (km²), the average slick thickness is estimated to be 0.1 millimeter (mm). Note that in estimating the area of the slick, sheen area should not be included (more on sheen in the next section) and some provision should be made for volume lost to evaporation.

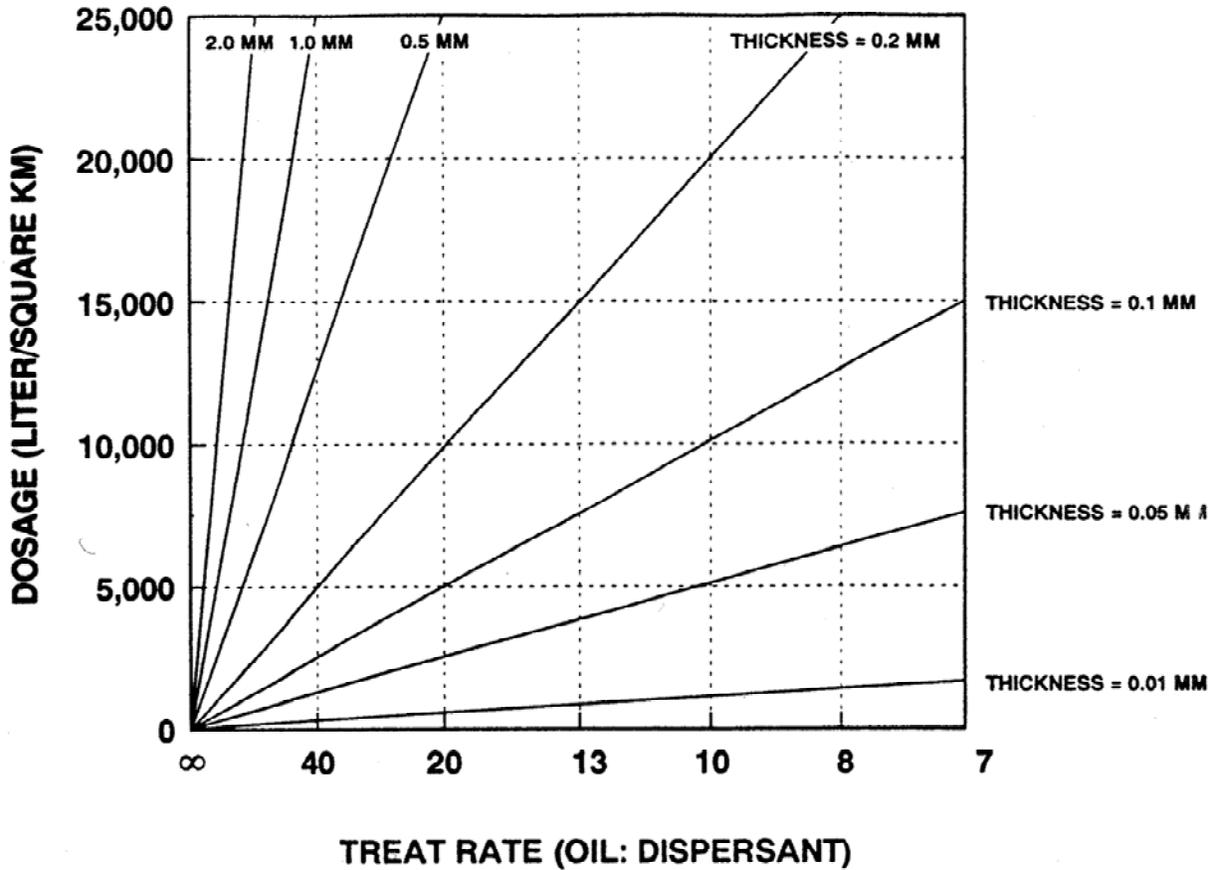


CONVERSIONS:
SQ. MILE = 2.59 x SQ KM
ACRE = 247 x SQ KM

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Figure 14.1 Determination of Slick Thickness when Area and Volume are Known

The estimated average slick thickness and the desired oil:dispersant treat ratio (the reverse of DOR) can be used with Figure 14.2 to determine the application dosage rate in either Liters/km² or U.S. gallons/acre. For example, for a slick thickness of 0.1 mm at a 1:20 oil:dispersant treat ratio, a dispersant application dosage rate of 5000 Liters/ km² would be selected, using Figure 14.2. This application dosage rate is equivalent to about 5.3 gallons/acre, using the conversion factor noted at the bottom of Figure 14.2 (multiply by .00107, or divide roughly by 1000).



CONVERSION:
DOSAGE (U.S. GALS/ACRE) = DOSAGE (LITER/SQ KM) x 1.07 x 10⁻³

Figure 14.2 Determination of Chemical Dispersant Dosage when Thickness is Known

In practice, identifying the actual thickness of the oil is a matter of best judgment. At present, there is no technique that accurately measures slick thickness so responders typically characterize oil thickness based on slick color. Remote sensing can give an indication of relative thickness of

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different areas of a slick. Applying dispersant to silvery or rainbow sheens (.001 mm or less) is unnecessary and a waste of chemical. Generally, a slick will become thinner the further it spreads from the source. So, dispersants are usually targeted on the dark thicker areas away from the edges.

Oil slick thickness is an important parameter to relate application dosage rate and DOR. For example, a dosage rate of 5 gallons/acre (~5,000 L/km²) applied to a slick with an average thickness of 0.1 mm, results in an average DOR of 1:20. Thicker slicks, e.g., 0.2 mm average thickness, would require proportionally greater dosage rates, e.g., 10 gallons/acre (~10,000 L/km²), to achieve the same 1:20 DOR. Alternatively, a dosage rate of 10 gallons/acre applied to a 0.1 mm thick slick would give an average DOR of 1:10.

A further complication arises from the unevenness of the slick thickness. As an illustration, assume that a dosage rate of 5 gallons/acre is applied to a non-uniform slick of 0.1 mm average thickness. Thinner areas of the slick will receive greater than the target dosage, while thicker areas will receive less. Depending on the actual thickness, the thicker areas could be significantly under-treated, which would result in much slower or incomplete dispersion. Therefore, thicker areas (which may be of the order of 1-2 mm thick and remain on the sea surface after a single spray application) may require additional spray treatments in order to ensure that adequate dispersant is applied. However, as mentioned above, many dispersants can be effective on various oils at higher DORs of 1:30 to 1:50, so field applications at a uniform rate could conceivably still be effective over a range of slick thicknesses. The advice of an experienced dispersant specialist is recommended in such situations. Such specialists are members of all of ExxonMobil's response teams.

These issues of thickness and treatment are discussed in greater detail in section 15.

14.3 Storage

When stored properly and protected from contamination, dispersants are for the most part extremely stable, and have been stored in stockpiles for decades without any significant deterioration. They should preferably be stored as supplied by the manufacturer in unopened drums or other suitable containers such as tote tanks. But once opened, it is important to replace the container's cap securely to prevent contamination from moisture and foreign matter and evaporative loss of solvents. Some dispersants are formulated with nitrogen- and phosphorus-containing nutrients to help accelerate oil degradation after dispersion. These are vulnerable to biological activity, especially if they become contaminated with water vapor, and should be stored in an extremely secure fashion to prevent intrusion by water and/or organisms.

For bulk storage, dispersants can be stored in mild steel, carbon steel, stainless steel, fiberglass, high-density polyethylene or polypropylene containers. Galvanized metal and aluminum containers are not recommended. Plastic tank linings are also generally not recommended because these materials can be affected by the solvent package in some dispersant concentrates.

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No unusual storage precautions are necessary to manage a dispersant stockpile. Most manufacturers of solvent-based dispersants recommend a storage temperature range of 40 to 100°F (4 to 38°C). Temperatures above 150°F (66°C) and below 0°F (-18°C) should be avoided. Storage should comply with prevailing local or international guidelines and fire prevention requirements and follow the manufacturer's recommendations.

Inventory management should follow a "first in first out" or FIFO approach with the oldest products being replaced with fresher batches at every opportunity. Sharing of stockpiles among response groups is encouraged because creating and maintaining a dispersant stockpile can be quite expensive. Additionally, when purchasing dispersants, the cost effectiveness of a particular product needs to be considered because there can be quite a range in the potency of the surfactants used and their concentration. Dispersants formulated to be effective on a broad range of oil types and on fresh and weathered crudes provide greater efficiency for stockpiles that may be needed for diverse spill situations. A low price may represent false economy if more dispersant must be used to achieve good dispersion for typical oils or the formulation is effective only on a narrow range of oil types.

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15.0 APPLICATION FUNDAMENTALS AND DELIVERY PLATFORMS

A major challenge in carrying out a successful dispersant operation is delivering the *proper* amount of dispersant to the oil. Improper or inadequate application is a leading reason why some dispersant operations have been unsuccessful over the past 30 years. Full dispersion requires sufficient dispersant to enable each oil droplet that is formed to be enveloped by at least a monolayer of surfactant to resist coalescence and ensure its stability in the water column. Also, the dispersed oil droplet must be small enough to remain suspended in the water column by turbulent mixing. Early on, testing determined that for a typical crude oil, that amount of surfactant corresponds to about 1 part of formulated dispersant for every 20 parts of oil. But as discussed in the preceding section, there are many factors and variables that can determine whether or not 1:20 DOR is too much or too little for a particular application.

ExxonMobil personnel, particularly Gordon P. Lindblom of Exxon Chemical Company, played a major role in the 1970s and 1980s in defining the important parameters that govern the effectiveness of dispersant delivery platforms. Much of the original fundamental work was documented in symposia and papers at oil spill conferences in the 70s and early 80s (see, for example, ASTM, 1977, and Lindblom, 1979). The principles and learnings developed then are still in use today and, although they continue to evolve, the fundamentals of application dosage rates have not changed dramatically in over 30 years.

15.1 Factors Affecting Application

The operational objective of any spray operation, be it by fixed-wing aircraft, helicopter, or vessel, is to efficiently apply the optimal amount of dispersant as small droplets over the slick area to be treated. Even with extensive planning and regular response training prior to a spill, applying the proper amount of dispersant involves complex decision making. Many of the factors that can affect effectiveness, such as oil viscosity and emulsification, have been discussed in sections 7 and 8. This section reviews additional physical challenges to an effective application. Awareness of these potential challenges is essential in delivering adequate dosages and maximizing effectiveness.

Film thickness. The largest uncertainty in determining the proper dosage application rate is the film thickness of the oil. Most application technology has been designed on a presumption (based on studies in the 1980s) that an oil slick will thin to a film thickness of the order of 0.1 mm within an hour or two (McAuliffe, 1989). That is the thickness that corresponds to a DOR of 1:20 at the conventional application rate of 5.3 gallons per acre. In actuality, responders to large spills probably rarely encounter a film thickness of 0.1 mm, but there is no way to know for sure because a device to accurately measure film thickness in the field has not yet been developed. This leaves room for considerable uncertainty since observers cannot see a difference between a slick of 1 mm and 2 mm.

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As reviewed in section 14, if the volume of oil spilled is known, an estimate can be made of the *average* film thickness by dividing that by the area of the spill, a value that can be determined through field observation. If a very large spill has not actually thinned to 0.1 mm but is in fact one or two orders of magnitude thicker (as was probably the case during the spray testing phase at the *Exxon Valdez* in 1989), then the dispersant will be seriously underdosed using conventional approaches and will therefore be less effective. Even if dispersion is occurring at the oil/water interface, spotters in the air will not be able to observe it due to the large amount of oil remaining above the dispersing interface. Only sub-surface water sampling or observation would be able to confirm effectiveness in such a situation, and that is very difficult.

Recommendation: If uncertain about film thickness, apply dispersant at conventional dosage rates (5 gallons/acre or 5000 Liters/km²) and monitor for effectiveness. If effective, consider cutting back on application rate in order to conserve dispersant supply. If ineffective, make a second application over the treated area at similar dosage. Conduct multiple passes, if necessary, until effectiveness is observed. Adjust the dosage based on test results to achieve the proper treatment. As the spill response continues, additional testing may be warranted to make necessary adjustments as the oil continues to thin and weather.

Film uniformity. Another uncertainty with respect to dispersant application is the distribution of the oil across the slick. Dispersant application settings, especially on large fixed-wing aircraft and on vessels, are set on the presumption that the oil will be uniform throughout. This is not always the case, especially if emulsification is occurring. In 1994 sea trials in the Norwegian sector of the North Sea, it was found that the large majority of the oil that did not evaporate—over 95% of the residual—was contained in less than 15% of the slick area (Lewis et al, 1995). The other 85% of the slick was comprised of sheen—oil with a thickness less than 1 micron (.001 mm).

Table 15.1 summarizes the quantity of oil contained in slicks as a function of oil thickness. Note the relatively minor amounts in sub-micron sheen. Spraying should not be conducted in areas of rainbow or silver color, the typical appearance of sheen areas. This is a waste of chemical as it overdoses the sheen and under-doses the thicker areas. The bulk of the spray generally should target oil located in areas that are deep brown or black. In cases where oil is concentrated in small pockets or in narrow windrows, it may be prudent to rely on delivery platforms with tighter targeting capability, e.g., boats or helicopters.

Recommendation: Prior to carrying out the first dispersant mission, use spotter planes to help define areas of thicker oil that should receive priority treatment. Planes equipped with *SatLoc* systems can map where the thicker areas are and then come back to spray them.

Table 15.1 Quantity of Oil as a Function of Appearance and Slick Thickness

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(ExxonMobil, 2005)

	Appearance/Approximate Thickness					
	Barely Discernible	Silvery Sheen	Rainbow Colors	Darkening Bands of Color	Brown or Black	Dark Brown or Black
Approximate Thickness (Microns) *	0.05	0.1	0.5	1 (.001 mm)	100 (.1 mm)	1000 (1 mm)
Area (m ²)	Liters					
100	<.01	.01	.05	.1	10	100
1,000	.05	.1	.5	1	100	1000
5,000	.25	.5	2.5	5	500	5000
10,000 (1 hectare)	.5	1	5	10	1000	10000
100,000	5	10	50	100	10000	100000
500,000	25	50	250	500	50000	500000
1,000,000 (1 km ²)	50	100	500	1000	100000	1000000
Area (ft ²)	Gallons					
1,000	< .01	< .01	.01	.02	2.5	25
10,000	.01	.02	.1	.2	25	250
43,560 (1 acre)	.05	.11	.53	1.1	107	1066
100,000	.1	.2	1.2	2.4	245	2450
500,000	.6	1.2	6	12	1224	12240
1,000,000	1.2	2.5	12.2	25	2450	24500
5,000,000	6	12.2	61	122	12240	122400
10,000,000	12	24	122	245	24500	245000
27,878,400 (1 mi ²)	34	68	341	682	68230	682300

* Typical averages based on numerous literature sources.

Note: Area of a spill is arrived at by multiplying the estimated length of the spill by estimated width.

Examples: 1000 m x 1000 m = 1 km²; 100' x 50' = 5,000 ft²

For Reference: 264.2 gal. = 1 tonne of oil

Spraying inefficiency. Some of the field tests carried out in the early days to test dispersant formulations achieved excellent dispersion by pre-mixing the oil and dispersant to make a perfectly uniform blend. When dispersant is applied from boats or aircraft, however, there is inherent inefficiency and loss of product that must be accounted for in planning the dosage. As a rule of thumb, the closer the spray is to the oil, the less the application inefficiency. In other words, as aircraft altitude rises, the more potential that the droplets will be diffused or blown off target and the resulting application rate at the oil slick will be affected. Agricultural and other aircraft that can fly lower than 50 feet have a better chance of achieving the desired application rates. Testing has shown excellent dose applications at 10-15 ft (3-5 m).

Alternatively, boats that apply dispersant from a height of just a few feet above the sea's surface achieve very good dosage distribution.

Recommendation. In setting spray rates to achieve a target dosage, always make allowance for spraying inefficiencies, depending on height above the oil.

Delayed action. In the research tests in which dispersant and oil were pre-mixed, the dispersion effect was always very spontaneous and visually striking. In actuality, dispersants may not begin

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to work until some time after application because, once the dispersant is applied, the surfactants require sufficient time to reach the region where they function, i.e., the oil/water interface.

Many factors control the time when dispersant effectiveness occurs, including dispersant formulation, sea energy, type of oil, thickness of oil, viscosity and general condition of the oil, etc. If responders are not aware that there could be a time delay, i.e., an induction period, a conclusion may be reached prematurely that the dispersant is not effective. As discussed previously, in the *Sea Empress* spill the Coastguard Agency's Marine Pollution Control Unit, accustomed to dispersant operations that were immediately effective and clearly observable from the air, reported no success with the dispersant application but measurements made in the sea with a fluorosensor showed that dispersion was actually occurring, but at a delayed rate (Harris, 1997). As noted earlier, dispersant operations proceeded successfully throughout the *Sea Empress* spill response.

Recommendation. Do not assume that if dispersion is not spontaneous and quickly observed, the operation is unsuccessful. This is especially true for emulsified and heavier oils, where dispersion may be delayed for prolonged periods (over 30 minutes). Observation/monitoring for effectiveness should be carried out for at least a half hour after application.

15.2 Factors Affecting Dispersant Droplet Size

An important requirement of dispersant application systems is that they deliver the dispersant in the right droplet size range. Years of experimentation have shown that the ideal volume median diameter (VMD) for a neat dispersant spray is about 500 microns (500 microns = 0.5 mm). The optimum size range is 300-700 microns. Drops that are too fine may drift off target and may not be available for the intended application density. Drops that are very large can fall right through thin oil films into the seawater, though studies at Ohio State University suggest that this may not be as much of an issue as previously thought because much of the dispersant re-surfaces at the oil/water interface and still remains with the oil (Ebert, et al, 2008) (see Figure 15.1). The factors most important to delivering the proper droplet size are the dispersant viscosity, the differential velocity affecting shear rate at the spray nozzles, and the size and configuration of the spray nozzles.

15.2.1 Dispersant Viscosity

In general, the higher the viscosity at the aircraft application temperature, the better, since viscosities that are too low will result in droplets that will be too fine. Many formulations containing significant levels of hydrocarbon solvents tend to have very low viscosities (some less than 10 centiStokes). In these cases, it would be expected that a large percentage of their aerial spray will be of very small droplets that are prone to drifting off target. Water-based products may experience evaporation, especially under 100 microns.

A

B

C

D

E

F

G

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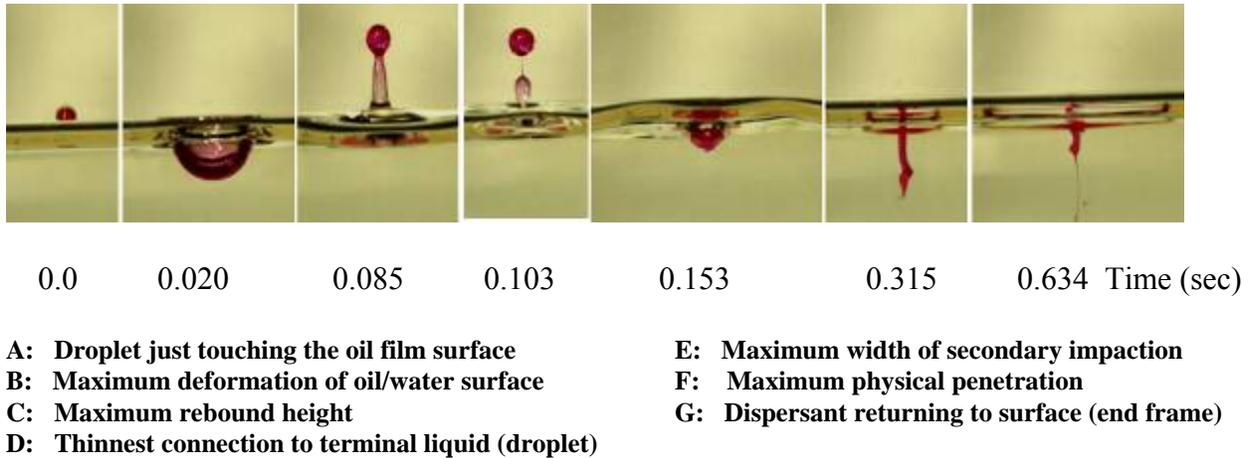


Figure 15.1 High-Speed Photography Showing a 3.21 mm Corexit 9500 Droplet Impacting a 2mm Thick Slick of Soybean Oil from a Height of 50.8 cm (20 inches) (Ebert et al, 2008).

Table 15.2 summarizes the impact of viscosity on drop size.

Table 15.2 Dispersant Viscosity Effect on Drop Size

Dispersant Fluid Viscosity (at application temperature)	Application Condition
≥ 60 centistokes (cSt)	<ul style="list-style-type: none"> • Best for aerial application at all speeds and heights
30 - 60 cSt	<ul style="list-style-type: none"> • Adequate if aircraft's ground speed is less than 100 mph (160 km/hr) and altitude is not over 30 ft (10 m)
< 30 cSt	<ul style="list-style-type: none"> • Not satisfactory for aerial application since a fluid stream is easily shattered by air shear • Produces extremely small size droplets, which are subject to excessive drift

15.2.2 Differential Velocity

Another important parameter affecting dispersant drop size and depositional efficiency from aircraft is the *differential velocity*, which is defined as the difference between the ground speed

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velocity of the aircraft and the exit velocity of the chemical through the nozzle. The greater the differential velocity, the smaller the mean diameter of the dispersant droplets. Tests over land in Arizona have shown that, if differential velocity is less than 250 ft/sec (150 knots), the resulting shear rate produces the appropriate droplet size distribution. The fluid exit velocity is given by the following equation:

$$\text{Fluid exit velocity (ft/sec)} = 0.41 (\text{GPM})/n d^2$$

where GPM = total system flow in US gallons per minute
n = number of nozzles
d = nozzle orifice diameter in inches

In the Metric system:

$$\text{Fluid exit velocity (km/hr)} = q/22d^2$$

where q = flow rate per nozzle in ml/sec
d = orifice diameter in mm

15.2.3 Nozzles

The size and number of nozzles affect the drop size and dosage. There are many nozzle sizes available with orifice diameters ranging from 0.15 to 0.8 in. (4 - 21 mm). There is no single nozzle applicable to all platforms. Properly-sized nozzles are required for each type of application. For aircraft application speeds of 150 knots, nozzles with orifices of 5 mm (.20 in.) to 8 mm (.315 in.) without nozzle tips or internal cores are best. They should be configured to discharge horizontally in the aft direction in order to avoid excessive shear that would create smaller drops.

Since agricultural spray planes normally use nozzles that are too fine for oil spill dispersant application, they must be replaced with nozzles with at least a 4 mm orifice. Helicopters also use nozzles with minimum 4 mm orifice. Boats applying dispersant diluted in a water carrier typically use 12 mm (0.47 in.) nozzles that produce a fan spray; however, one nozzle size may not meet all the requirements for droplet size and application rate so manufacturers sometimes provide several nozzle sizes to accommodate the large range of conditions likely to be encountered (S.L. Ross, 2004). Recent tests have shown that, with proper pumps and nozzles, the pressure and discharge rate do not change greatly with boom length so it normally should not be necessary to vary nozzle size along the boom in order to achieve uniform spray. ASTM F 1460 (ASTM, 2006) provides helpful information for calibrating spray systems.

15.3 General Guidelines on Application Techniques

Dispersants can be applied from platforms ranging in size and speed from small workboats to large, multi-engine aircraft. In general, workboats are more suitable for treating minor spills in

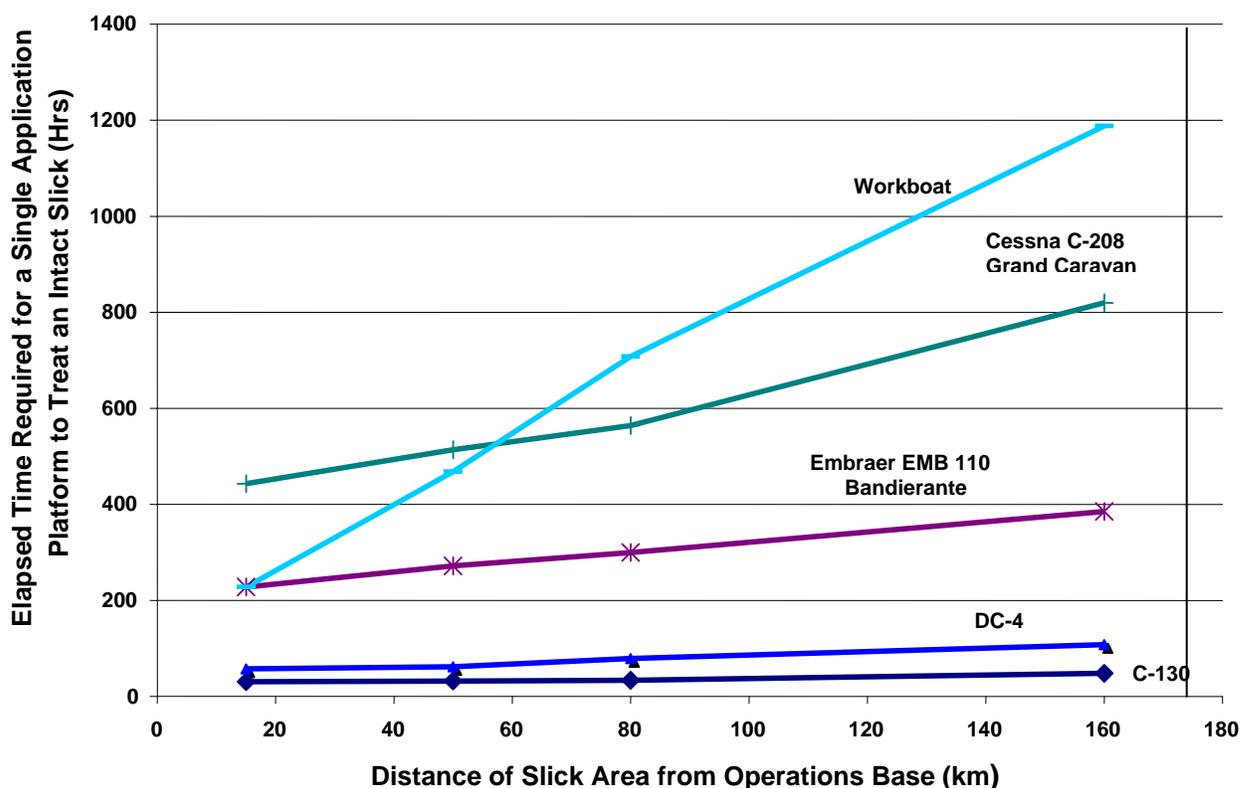
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harbors or coastal areas because of their availability and cost. They may also represent the only option in busy port areas where aircraft may be prohibited for safety reasons. Large, multi-engine airplanes are best for handling large, offshore spills. Their advantage lies in the high coverage areas that are possible.

Small airplanes and helicopters are suitable for treating smaller spills and spills that require more targeted application due to variable slick thickness or oil distributed in narrow windrows or patches. Figure 15.2 shows the relative times required by the various application platforms to chemically treat a 24,000 barrel (bbl) spill, assuming no evaporation loss, an average thickness of 0.1 mm, area slick size of approximately 20 mi² (about 50 km²) and a dose rate of 5.3 gallons/acre (5000 liters/km², DOR = 1:20) and a pass length of 4 nm. The time required is plotted as a function of the distance of the slick area from the operations base. While a workboat would take hundreds of hours to treat the entire slick, larger aircraft require less than 50 hours for a slick 100 km (60 miles) away.

The *World Catalog of Oil Spill Response Products* provides a listing of dispersant application equipment and vendors (SL Ross Environmental Research, 2004, Chapter 7). ExxonMobil funded the original edition of this important and useful catalog by Robert Schulze in 1986. **Current (as of the date of publication of this manual) contact addresses and phone numbers for some vendors are provided in Appendix B.**

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**Figure 15.2 Chemical Dispersant Application Logistics for a 24,000 bbl Spill –
Effect Of Operating Distance on Treatment Time for Various Platforms
(Bases: 5.3 Gal/Acre, 1:20 DOR, 4 nm Pass Length)**

The utility of large aircraft versus small airplanes, helicopters and workboats for dispersant spraying is shown in Tables 15.3a (in Metric units) and 15.3 b (in English units) which summarize typical airplane and workboat characteristics. The payload, speed, and typical number of missions per 12 hour day greatly favor applying dispersants by aircraft.

Note: The data shown in Tables 15.3a and 15.3b for number of daily missions and amount of dispersant applied to a slick four nautical miles (NM) long differ markedly from earlier versions of these Dispersant Guidelines. Recent studies and experience have shown that the original estimates made in the 1970s and 1980s were too optimistic. In particular, a better understanding of the time needed for turn-around between sorties, including that for landing and takeoff, has been gained since the last edition, thanks in large part to studies funded by NOAA and MSRC. See NOAA’s revised Dispersant Mission Planner at <http://response.restoration.noaa.gov>.

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Table 15.3a Typical Aircraft and Workboat Characteristics (Metric)

Characteristics	Lockheed Hercules L-382/ C-130 w. ADDS ¹ PACK	Douglas DC-4	Air Tractor AT-802	Smaller Planes, e.g., Beechcraft, CASA, Cessna, Bandierante	Bell Helicopter	Typical Large Workboats
Payload (Liters)	20,000	7600	3,000	800-1,900	680	2,100-6,500
Turnaround Time With or Without Refueling (Minutes)	60-75	30-60	20	30-60	15	25-75
Max Avg. Transit Speed (km/hr)	350	350	310	370-400	210	10-17
Spray Speed (km/hr)	280	260-295	210-260	300	200	2-15
Repositioning Speed (km/hr)	325	295	260	300-370	200	4-17
Time to Initiate a 180° Turn (Min.)	1	1	0.5-1	1-2	1	2-10
Neat Dispersant Pump Rate (Liters/Minute)	2,400-3,000	1,890-2,270	570	760-1,900	400	60-150
Typical Swath (Meters)	25-60	25-60	30-40	18-27	10-15	15-30
Minimum Runway Length Required (Meters)	1,830	1,525	580	790-1,500	NA	NA
Average Number of Missions per 12 Hr for 7.4 km (4 NM) slick / Liters of Dispersant Applied every 12 Hr						
DISTANCE (km)						
15	6 / 120,000	9 / 67,000	16/ 48,000	9 / 17000 ⁽²⁾	23 / 16,000	3 / 20,000 ⁽³⁾
50	6 / 120,000	7 / 53,000	12/ 36,000	8 / 15,000 ⁽²⁾	14 / 9500	1.5 / 10,500 ⁽³⁾
80	5 / 100,000	6 / 45,000	10 /30,000	7 / 13,000 ⁽²⁾	10 / 7000	1 / 6500 ⁽³⁾
160	5 / 100,000	5 / 38,000	7/ 21,000	6 / 11,000 ⁽²⁾	6 / 4000	NA
240	4 / 80,000	4 / 30,000	5/ 15,000	5 / 9500 ⁽²⁾	4 / 3000	NA

⁽¹⁾ ADDS = Airborne Dispersant Delivery System

⁽²⁾ Based on Bandierante

⁽³⁾ Based on 6500 Liter Payload

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Table 15.3b Typical Aircraft and Workboat Characteristics (English)

Characteristics	Lockheed Hercules L-382/ C-130 w. ADDS ¹ PACK	Douglas DC-4	Air Tractor AT-802	Smaller Planes, e.g., Beechcraft, CASA, Cessna, Bandierante	Bell Helicopter	Typical Large Workboats
Payload (Gallons)	5280	2000	800	210-500	180	550-1700
Turnaround Time With or Without Refueling (Minutes)	60-75	30-60	20	30-60	15	25-75
Max Avg. Transit Speed (Knots)	190	190	170	200-215	113	10
Spray Speed (Knots)	150	140-160	115-140	160	110	1-8
Repositioning Speed (Knots)	175	160	140	160-200	110	2-9
Time to Initiate a 180° Turn (Min.)	1	1	0.5-1	1-2	1	2-10
Neat Dispersant Pump Rate (Gallons/Minute)	630-800	500-600	150	200-500	100	16-40
Typical Swath (Feet)	80-200	80-200	100-130	60-90	33-50	50-100
Minimum Runway Length Required (Feet)	6000	5000	1900	2600-5000	NA	NA
Average Number of Missions per 12 Hr for 4 NM slick / Gallons of Dispersant Applied every 12 Hr						
DISTANCE (mi)						
9	6 / 32,000	9 / 18,000	16/ 12,600	9 / 4500 ⁽²⁾	23 / 4200	3 / 5300 ⁽³⁾
30	6 / 32,000	7 / 14,000	12/ 9500	8 / 4000 ⁽²⁾	14 / 2500	1.5 / 2800 ⁽³⁾
50	5 / 26,000	6 / 12,000	10 / 8000	7 / 3400 ⁽²⁾	10 / 1800	1 / 1700 ⁽³⁾
100	5 / 26,000	5 / 10,000	7/ 5500	6 / 3000 ⁽²⁾	6 / 1000	NA
150	4 / 21,000	4 / 8000	5/ 4000	5 / 2500 ⁽²⁾	4 / 800	NA

⁽¹⁾ ADDS = Airborne Dispersant Delivery System

⁽²⁾ Based on Bandierante

⁽³⁾ Based on 1700 Gal. Payload

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Spreadsheet models are available that can aid in estimating the time and operational parameters of various application techniques for a given spill scenario. For example, the NOAA Dispersant Mission Planner is an excellent model that was recently updated based on consensus input from industry and government sponsors in the US and spray aircraft operational data confirmed by the aircraft pilots. Examples of input data needed include spill site data (e.g., quantity of oil spilled, area of oil slick, distance of spill from loading airport/dock used to stage operations, target DOR, etc.) and application platform characteristics, such as aircraft speed, dispersant capacity, application rate, swath width, time for reloading, etc. The model output provides estimates of the amount of dispersant needed, time to complete the spray operation, number of missions needed and other operational parameters.

For nearshore dispersant applications where shoreline impact is imminent, availability and time factors must also be considered in selecting an application method. For example, if the leading edge of a slick is 2 kilometers (1.2 miles) from the shoreline and advancing toward the shoreline at a rate of 0.1 km per hour, a maximum of 20 hours is available for both transit to the spill site and the spraying operation. With such a narrow window of opportunity, it is important that spraying operations be initiated along the leading edge of the slick to provide the best chance of avoiding or reducing shoreline impact.

If the slick in the above example is 4 km (2.5 mi) wide (along the leading edge) and 1 km (0.6 mi) long, an average dispersant treatment rate of 0.4 square km per hour (about 100 acres) can prevent the slick from progressing toward the shore. (This "zero progress" treat rate is calculated by multiplying the width of the slick along the leading edge times the rate of advance.) In this example, it would take 10 hours to treat the entire slick, but the slick would not progress toward shore during this time.

15.4 Aerial Application

The average dispersant treatment rate (amount of area covered per unit time) will vary for each application platform, depending on the specific logistics of the spill and operational and application characteristics of the aircraft. Aircraft, however, will generally always give significantly higher average treatment coverage areas than boats (e.g., 0.5 – 1.0 square km per hour for large aircraft vs. 0.02 – 0.1 for the largest workboat).

Aircraft allow efficient dispersant treatment of spills at greater distances from an operations base than is practical with workboats. In the scenario depicted in Table 15.1, workboats cannot complete a single mission in 12 hours if the spill is more than 80 km (50 mi) offshore, due to their much slower speed of transit and dispersant application. Although the area covered per unit of time by aircraft is greatly increased over that of workboat spraying techniques, the time for spraying each load of dispersant is limited to only a few minutes. Because of the low ratio of spraying time to total time per mission, the transit time, repositioning time over the slick, and reloading plus refueling time must be considered in estimating the total time to treat all or part of

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a spill by aircraft. This type of information is included in Table 15.3 and in the revised NOAA Dispersant Mission Planner.

A typical aerial application by multi-engine aircraft (C-130A) is illustrated in Figure 15.3. Tests in the early 1980s showed that optimum effectiveness is achieved at a plane altitude of 15.2 m (50 ft). Additional testing in 1992-93, sponsored by the Marine Spill Response Corporation (MSRC), Oil Spill Response Ltd. (OSRL), the Texas General Land Office (TGLO), ExxonMobil and others showed that somewhat lower efficiencies will be achieved at higher altitudes (100-150 ft) (Giammona, et al, 1994). Further testing by MSRC in 2006 has shown that between 50 and 100 feet (15-30 m) effective application can be conducted with little variation in dosage, swath, and mean diameter. Careful and complete calibration of aerial systems and spray testing at field conditions is essential for maximum success. **When applied by aerial spray, dispersants are always applied neat (undiluted).** Neat application maximizes the dispersant-carrying capacity of the aircraft and oil that can be treated per sortie.



Figure 15.3 Aerial Application of Chemical Dispersants from MSRC's C-130A, Supplied by International Air Response, Inc. (courtesy of MSRC)

Effective use of aircraft requires spray booms, nozzles, and pumps capable of providing a controlled and uniform application of dispersant chemicals across a desired swath, i.e., to a given "target" area. To achieve this, the spray system must include an accurate flowmeter and fluid pressure read-out, and produce a droplet size distribution that is not so small as to cause loss of material by wind drift. Droplet size and swath are not completely independent in that production

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of a spray with the appropriate droplet size minimizes misting (i.e., formation of droplets so small that their deposition is disturbed by minor air turbulence) and also results in a more uniform swath. For reference, ASTM F1738-96 (2007), *Standard Test Method for Determination of Deposition of Aerially Applied Oil Spill Dispersants*, may provide useful background.

In aerial spraying, an important consideration is "*depositional efficiency*," i.e., the proportion of the spray that falls on the target area within a reasonable swath. To aid in achieving this, dispersants with viscosities of 60 centiStokes or more are recommended. Dispersants with extremely high viscosity, however, could lead to flow problems in very cold weather using conventional application equipment. However, tests on products such as Corexit 9527 have shown no application problems due to viscosity effects for aircraft and vessel application systems even at temperatures below 0°F (-18°C).

Dispersant concentrates are optimum for aerial application, both because of their higher viscosity and also because less total material is required per unit area of slick. Except for very large spill areas, crosswind aerial application is not recommended because the dispersant will have a tendency to drift off target, thus lowering depositional efficiency. Also, the swath will be wider, possibly resulting in areas of inadequate treatment rate. As dose rate, speed of the aircraft, and swath are increased, the required pump rate may become the first limiting factor. In addition, the size of the aircraft required for transport of the necessary equipment and dispersant could also become limiting.

For large spills, or for those at sites far from an operations base, multiple airplanes may be necessary to treat an oil slick with greatest efficiency. Also, a spotter plane operating at an altitude of several hundred feet is necessary to direct large aircraft to the thicker oil areas, as slicks are difficult to spot at the low altitudes used during application and it is even more difficult to discern thick from thin areas of oil under these conditions. With multiple aircraft, one can fly higher and spot for the other, taking turns applying the dispersant. Aircraft application may be relatively expensive per unit of time, but the ability to do the job faster than workboats, a reduced number of personnel during the operation, and avoidance of long-term costly shoreline cleanup that might occur if aircraft are not used, can make aircraft application cost-effective in the long run.

As with all forms of oil spill response, the major objective of dispersant-based treatment is to quickly remove the slick from the water surface and prevent spilled oil from impacting shorelines, other sensitive areas, or bird populations. When shoreline impacts are imminent, spray efforts should concentrate on the leading edge of the thicker portion of the slick that threatens sensitive areas. Remote sensing systems, such as infrared cameras, are available to help determine the relative thickness of different areas of a slick so that dispersant may be applied as effectively as possible. It should be emphasized again that **treating areas of light sheen generally offers minimal environmental benefit for the allocated spill response resources and may be a waste of dispersant.**

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While it is desirable that spraying of dispersant be conducted in water as deep as possible, treatment should not necessarily be prohibited if a slick is in shallow water because shoreline impacts will almost surely occur if action is not taken. In every case, the response team must consider the environmental, economic and other issues between chemical dispersion of the oil, and shoreline impact.

15.4.1 Fixed-Wing Aircraft

A variety of fixed-wing aircraft can be used for dispersant application. Airplanes are available with chemical tank capacities ranging from 200 to 5,000 U.S. gallons (0.8-21 tonnes). The 5,000 gallon tank commonly in service is called the ADDS PACK (Airborne Dispersant Delivery System), a robust application system developed in the 1970s with considerable ExxonMobil involvement. The ADDS PACK can be rolled onto a Hercules L-100 or C-130C or later aircraft to provide the maximum delivery capability possible with a single platform.

Properly equipped multi-engine airplanes are not widely or readily available for rapid response to an emergency. In order to rely on this type of dispersant application system, dedicated planes may be required, or arrangement for guaranteed response times negotiated. Since these aircraft will be required to operate at low altitudes, and may have to travel great distances from their home base to the spill site, the following criteria should be considered for safe operation and rapid response:

- Sufficient navigation and satellite communications equipment installed, and complete navigation charts available
- Experienced crews trained in low altitude techniques and backup crews to sustain operations
- Accurate radar altimeter to eliminate problems in visually judging altitude over water
- Inertial navigation system (INS) to aid in accurately positioning and repositioning the aircraft over the slick. **Even in the case where INS is available, a spotter aircraft with the capability to communicate with the spraying aircraft is still recommended.**
- Application spray navigation and recording equipment

Light airplanes normally used for agricultural spraying, such as the Piper Pawnee, Cessna AgTruck, AirTractor, Ayres Thrush, or AgCat, are acceptable for treating spills, provided they are equipped with proper spray nozzles, pumps, and flowmeters. Usually, these aircraft are employed to spray fertilizers and pesticides from low altitudes at extremely low dosages and most of the nozzles used for these purposes produce a very fine spray that is not adequate for dispersant application. A D10-46 orifice (diameter 0.39 cm or 0.156 in.) or larger is required for smaller planes. Figure 15.4 shows an Air Tractor in tests at Alpine, Texas in 1993 using the proper nozzles. Prior to being used for dispersant spraying, the tanks should be completely cleaned.

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Figure 15.4 AirTractor (800 Gallon Capacity) Applies Dispersant at Alpine, Texas Test

Nozzle bodies with check valves, but without nozzle tips or internal cores, having discharge tubes of at least 3/16 inch (4.7 mm) diameter, are recommended for faster airplanes such as the Canadair CL-215, the DC-4 and DC-6, and large cargo planes such as the C-130 Hercules because these will require higher dispersant pump rates. As mentioned earlier, to obtain the most even coverage, nozzles on all aircraft should be installed to discharge directly aft to avoid excessive wind shear across the fluid orifice. Figure 15.5 is a photograph of a Southern Air L-100 during the 1993 field tests in Alpine, Texas. Dye has been added to the dispersant as a means of measuring the deposition density on the ground. Dispersants are normally colorless. Figure 15.6 is a close-up view of a typical spray nozzle on an aircraft spray boom.

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Figure 15.5 Aerial Application of Corexit 9527 (Dyed Blue) from Southern Air L-100 Using ADDS PACK System in Alpine, Texas Test (Courtesy of Shell)



Figure 15.6 Close-Up View of Spray Boom Nozzle (BETE NF 70) (Courtesy of MSRC)

In recent years, many versatile smaller fixed-wing aircraft have been modified for dispersant application and have found wide acceptance. As a general guide, the smaller aircraft should not

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use nozzles with external orifice diameters smaller than 4 mm (0.156 in). The small planes typically have no more than 30-35 operating nozzles. Some of the more popular ones are the Beechcraft King Air 90A, the CASA C-212-200 Aviocar, the Cessna C-208 Grand Caravan, and the Embraer EMB 110 Bandierante. As an example, OSRL has a Bandierante on standby in Western Africa (see Figure 15.7). The range of capabilities covering all these aircraft is summarized in Tables 15.3a and b.



Figure 15.7 Embraer Bandierante Spraying Dispersant (Courtesy of OSRL)

15.4.2 Helicopters

Helicopters can be fitted with integral spray units designed especially for a particular helicopter model or, more typically, they can use slung buckets equipped with spray booms and a pump (Figure 15.8). The bucket units are available in several sizes from 100 to 800 gallons (378-3,000 liters), are more versatile than the integral systems, and do not require lengthy installation or a dedicated aircraft. While larger helicopters are required for the larger buckets, the actual volume of material that can be carried depends on each helicopter's payload limitation and the distance of the spraying operation from a refueling base.

While applying dispersants, helicopters should not hover over a slick but rather fly forward at speeds of between 60 to 80 knots (69-92 mph, 111-148 km/hr) (Figure 15.9). When helicopters

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hover, or fly at low speeds, the rotor's downwash will produce excessive turbulence that will disrupt dispersant deposition. As forward, translational speed increases, the rotor acts essentially as a wing, and turbulence decreases dramatically, permitting normal spraying. Nozzle selection and the number of nozzles used are especially important for optimizing helicopter systems, because the effect of air shear will not be as important at speeds less than 100 knots. An orifice diameter of D 10-46 (0.39 cm, 0. 156 in.), or larger, is generally required.

When applying dispersants from a slung bucket on a helicopter at very low temperature (less than 0°F, -18°C), higher viscosity dispersants may require recalibration of the spray equipment, per ASTM F 1460 (ASTM, 2006).



Figure 15.8 Helicopter "Slung Bucket" Spray System



Figure 15.9 Helicopter Applying Chemical Dispersants Using the "Slung Bucket" Spray System

15.5 Vessel Applications

The methods for dispersant application from boats include spraying through a set of nozzles fixed on outboard spray booms, from fire monitors and through use of specially-designed single nozzle application systems. Boats of various types (workboats, tugs, barges, trimarans, etc.) are widely used as platforms from which to apply dispersants. However, some are relatively slow in transit to the spill site (e.g., less than 10 knots [11.5 mph, or 18.5 km/hr]) and during dispersant application (typically 3-5 knots advance speed though 8 knots has been reported to be do-able). Also, they cover a limited swath with their spray pattern. Only relatively small spills can be treated adequately in this manner even if a reloading facility is near.

Vessels do offer certain advantages over aircraft systems, including ready availability in port and marine terminal areas, lower cost, ease of deployment, high degree of spray control, and accuracy. To be most effective, vessels should (1) have sufficient dispersant payload or the ability to be re-supplied so that return trips to the staging area are not required, (2) be rapidly mobilized shortly after dispersant use approval, and (3) be located close enough to the spill scene (no more than 10 to 20 nautical miles [17-33 km]) to arrive within the required time when dispersant use is still effective. Installation of booms and loading of dispersant can be cumbersome and should be drilled.

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Operationally, vessels at a spill site provide the ability to spend a greater percentage of time applying dispersant to thick portions of oil slicks in one pass, without the need to turn around and re-position as is required for aircraft. This is a critical aspect of dispersant use for oil spills, since oil spills do not spread uniformly. Therefore, vessel dispersant application should not be overlooked, as it can sometimes be a viable and effective option for sustained dispersant application in certain oil spill situations. When aircraft are prohibited, vessels are the only option.

Table 15.4 summarizes some advantages and disadvantages of vessels for dispersant application.

Table 15.4 Vessel Dispersant Application Advantages and Disadvantages Compared to Air Application (based on Motolenich-Salas and Clark, 2005)

Advantages	Disadvantages
<ul style="list-style-type: none">• Vessels are widely available in many areas where oil is transported• Vessels can be quickly deployed from local ports and offshore operation areas• Mixing energy from vessel motion can improve effectiveness• Lower cost• High endurance; large vessels can remain on-scene overnight• Better targeting of thicker parts of oil• Can be used on small spills in harbors or congested areas where aircraft may be prohibited	<ul style="list-style-type: none">• Areal coverage rate is much lower due to lower encounter rate• Locating oil slicks can be difficult without overhead aircraft support• Slow transit speed can mean long delays in arrival at the spill site• Slow spraying speeds of 3-8 knots• Requires a supporting dispersant storage barge or vessel• Higher possibility of inadvertent spraying of personnel on board• Greater possible exposure to any remaining hydrocarbon vapors

S.L. Ross makes the case that boat applications have their greatest advantage versus aircraft when targeting small high-thickness slicks (Ross, 1998). In the case discussed earlier where much of the oil is concentrated in a small area of total slick, a vessel system could be preferable because large amounts of dispersant can be targeted specifically on the thick patches. However, positioning in the thickest oil is a challenge and will likely require overhead aircraft spotter support. Large aircraft that are designed for uniform spray would be hard-pressed to focus application to specific patches of thick oil. Even if they could, the logistics of applying the larger amounts of dispersant required are much more challenging for aircraft than for vessels.

15.5.1 Workboat Spray Boom Systems

The critical factor in efficient and effective application from workboats is the design of the application system. Boat-spraying systems were originally developed by the Warren Spring Laboratory (WSL) in the UK to make chemical dispersant spraying more controllable. These systems were especially useful for applying undiluted conventional hydrocarbon solvent-based

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dispersants at very high doses (35 to 95 US gallons/acre or 327 to 888 Liters/hectare). The WSL units employed pumps of 10 to 24 US gallons/min. (26 to 91 Liters/min.) capacity, operating at very low pressures. The agitation required to promote dispersion after spraying the neat dispersant formulations was provided by trailing wood "breaker boards" ("5-barred gates"). This required that the spray booms be mounted toward the rear of the vessel, often aft of the point where the bow wave breaks from the hull, causing some dispersant spray to miss oil that had been pushed away. The towing of "breaker boards" reduced the top speed significantly. The WSL system was later modified to apply newer dispersant concentrates diluted with seawater.

Many further improvements have been made in recent years in the design of dispersant-spraying equipment for boats, and a number of commercial units have such features as spray booms that do not require overhead rigging, low-drift nozzles, electric-start pumps, and flowmeters. Spray systems that apply dispersant neat are ideal for extremely thick slicks. For most slicks, however, water-dilution systems which provide a 5-10% dispersant concentration are suitable. Practically all modern non-hydrocarbon dispersants are formulated to be diluted with seawater during application, since they are active at very low dosage (2 to 10 U.S. gallons/acre, 19 to 94 Liters/hectare). A seawater pump with a capacity of 50 to 150 US gallons/min (189 to 568 Liters/min), operating at a pressure of at least 80 pounds per square inch (550 kPa), allows for easy chemical addition by eduction into the water stream. The mixture of dispersant and seawater is then discharged through booms via numerous nozzles.

In a typical installation, the booms are mounted as far forward as possible to avoid the bow wave. Because of variations in hull construction, the bow wave may break from the hull anywhere from the prow to near mid-ship and will move forward with increasing boat speed. Boat speeds for spraying operations can range from 1 to 10 knots (2.3 to 11.5 mph, 3.7 to 18.5 km/hr), with 3-5 knots being a preferred range for most systems to achieve the target dosage. Because an oil slick will be moved aside by the bow wave, spray booms mounted too far behind the breakpoint will provide less effective coverage.

The spray nozzles must be sized to the pump rate and pressure and should give a uniform spray of droplets—not a fog or mist. The spray pattern should be flat, striking the water in a line perpendicular to the direction of the boat's travel. The nozzle's spray angle should be such that the fan-shaped sprays from adjacent nozzles overlap above the water surface, and the inboard spray strikes the hull above the waterline. To get a consistent dosage across the entire length of boom, the spray fans should intersect close to the mid-point between nozzles. This is illustrated in Figure 15.10.

Any nozzle arrangement that provides this desired spray configuration is acceptable. If required, the booms can be stabilized by attaching rigging at two or three points along each boom and running stays from each point overhead, forward, and aft. Figure 15.11 illustrates a bow-spray system in operation with incomplete spray overlap.

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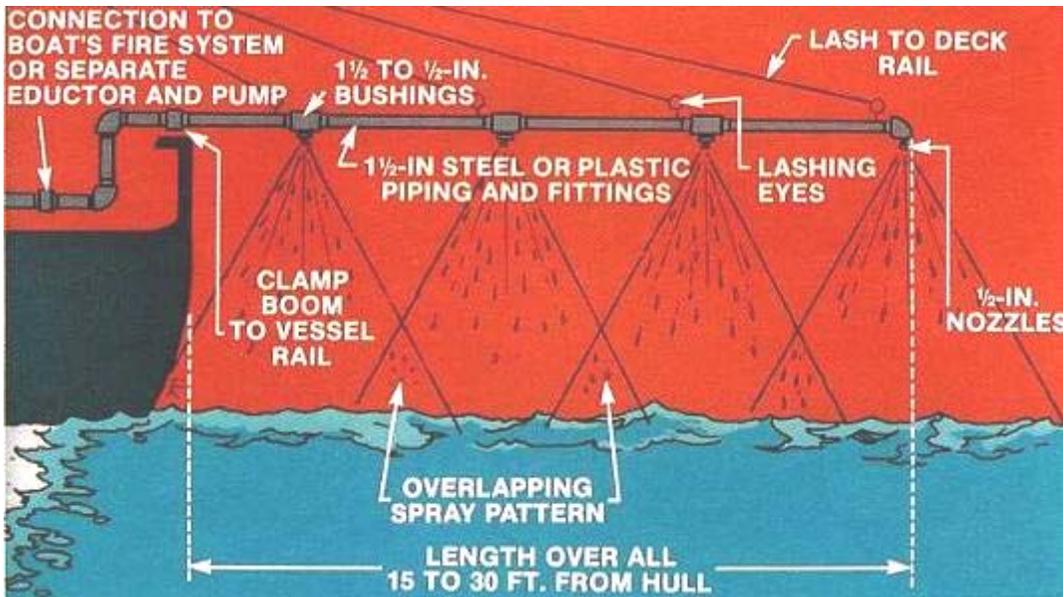


Figure 15.10 Example of Boom Arrangement for Tugs and Workboats



Figure 15.11 Workboat Spray Boom in Operation...Note Poor Overlapping

Vessel-mounted spray units can be permanent or portable, and booms can be of any practical length. It is preferable that systems be designed for a particular vessel and remain on that vessel. If the spray system is to be used on different vessels, the portable spray systems should include sets of spare nozzles having both different spray angles and flow rates. These extra nozzles are

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important for flexibility to change booms in order to be compatible with a variety of hull designs, and differences in inter-nozzle spacing and distances above the water.

Portable systems should be designed for rapid deployment. This means that the number and size of boom sections and nozzles required to optimally equip designated vessels should be pre-calculated. In addition, spray booms should not require extensive rigging, masts, or welded attachments. All units should be equipped with accurate flowmeters for dispersant addition and for water flow if an eductor is to be used. If portable pumps are not available, or are of inadequate size or capacity, dispersant concentrates can be educted into the water from the boat's firefighting system (if available) and the mixture discharged to the spray booms. **It is recommended that the performance of any unit be determined in advance under typical operating conditions in order to have a firm confidence in dispersant dosage control.** ASTM standard F 1460-07, *Standard Practice for Calibrating Oil Spill Dispersant Application Equipment Boom and Nozzle Systems*, can be helpful in this regard.

Dispersant dosage per unit area is affected by changing swath, boat speed, and pump rates. Published pump curves, tables of nozzle output vs. pressure, eductor percentage settings, and even calculated swaths are only general indicators to be used for guidance. While water can be used for calibration of units designed for application of diluted dispersants, for best results the dispersant should be employed for calibration of eductors (and for pumps when undiluted chemical is to be sprayed). It is especially important that eductors be properly cleaned and maintained and frequently recalibrated. Figure 15.12 shows a boom with uneven spray distribution under testing.



Figure 15.12 Uneven Spray Distribution During Test

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Hydrocarbon solvent-based dispersants can lose effectiveness when diluted with water and applied at DORs less than 1:20. Therefore, it is recommended that these types of dispersants should be reserved only for use with equipment that can apply them neat. Spray systems for undiluted dispersant require a much lower pump rate than those using dispersant addition to a water carrier. Nozzles must be properly chosen and sized for the lower volumes used.

15.5.2 Effectiveness of Corexit 9500 When Applied in Dilute Stream

Corexit 9500 can be applied as a diluted stream. In 2001, S.L. Ross published a paper summarizing several years of studies on vessel-based dispersant applications (Ross, et al, 2001). In that paper, the authors cited data which indicated that Corexit 9527 was preferable to Corexit 9500 when applied diluted in a water stream. Since then, there has been much confusion as to whether or not Corexit 9500 should be applied in a dilute sea water stream, much of it based on misinformation. The results that caused a stir are shown in Figure 15.13. Though Corexit 9527 was effective applied dilute at a DOR of 1:70, the effectiveness of diluted Corexit 9500 dropped off at 1:40. However, at a conventional ratio of 1:20-30, Corexit 9500 performed well in the Ross tests. The difference in performance is understandable as the solvent in Corexit 9527 is completely compatible with water whereas one of the solvents in Corexit 9500 is hydrocarbon-based.

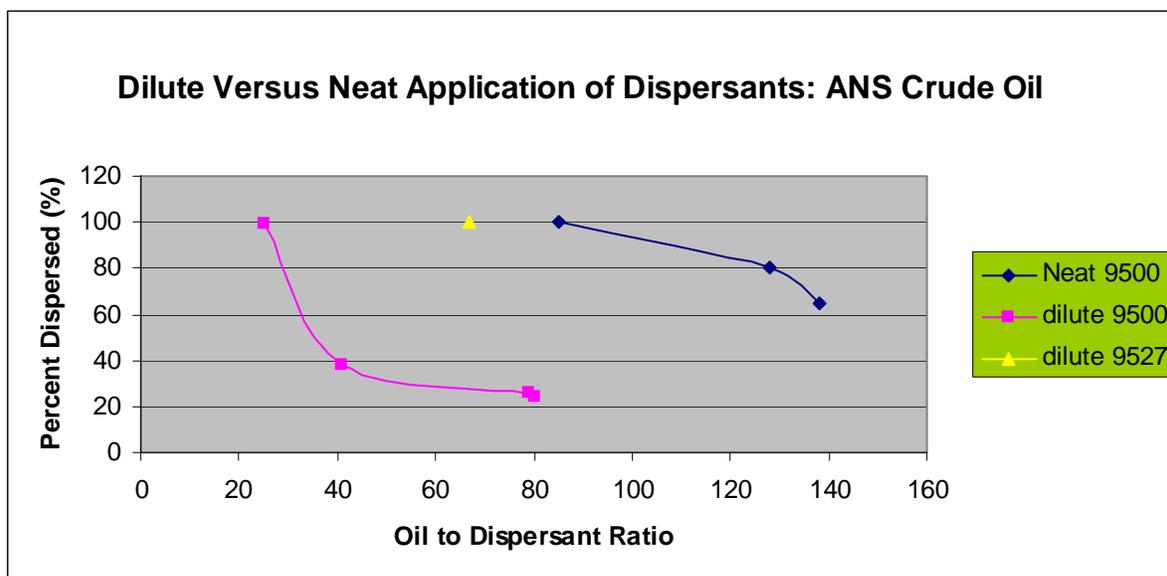


Figure 15.13 S.L. Ross Results With Dilute Corexit Dispersants (from Ross, et al, 2001)

In later studies at S.L. Ross, funded by ExxonMobil, it was found that the observed drop-off was crude-specific. The reduction in effectiveness did not occur for Hibernia or South Louisiana crudes. Also, at the 1997 *Captain* platform spill in the North Sea, Corexit 9500 successfully dispersed oil at a DOR of 1:100 when applied diluted to 7.5% (see section 16). Current thinking

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is that, as long as Corexit 9500 is applied at a DOR of 1:30 or more, it should be effective whether applied neat or diluted, regardless of crude.

15.5.3 Fire Monitor Systems

An alternative to spray booms is to use installed or portable fire monitors (Figure 15.14). The monitor nozzle should be aimed 30-40 degrees above the horizontal in order to direct the spray over a greater area and to ensure application via droplets (resembling rain), rather than a straight high-pressure stream. A straight high-pressure stream will likely pass directly through the slick, and may enter the water with minimal effect on the floating oil, although recent data at Ohio State University (Figure 15.1) shows that dispersant may resurface under the slick and still provide some degree of efficacy (Ebert, et al, 2008). Adding a "break-up screen" (e.g., a coarse 4 mesh screen) loosely fitted over the end of the nozzle will spread the spray over a greater area.



Figure 15.14 Workboat Fire Monitor Applying Dispersants

Some loss of effectiveness compared to neat application from a conventional dispersant application boom can be expected with a fire monitor application, particularly at DORs lower than 1:30. However, a boat equipped with two fire monitors can cover about 3 to 4 times the area of a boom-equipped boat. Fire monitors may be more suitable in situations where treating all of the spilled oil quickly is more important than achieving the highest effectiveness for each gallon of dispersant used. Prior work on the design and development of the application of dispersant by

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fire monitors can provide additional guidance for their use (see, for example, Belore and Ross, 1999; Chen, 1999).

15.5.4 Single-Point Dispersant Spray Systems for Vessels

Single nozzle systems designed for dispersant application of undiluted dispersant are a recent concept. ASTM Standard F 2465-05, *Standard Guide for Oil Spill Dispersant Application Equipment: Single-point Spray Systems*, provides a thorough review of this new application technique. These systems are designed to provide larger swath widths than spray arm systems and claim much-improved targeting capability. Single nozzle systems are said to be simple to install, maintain, and operate, and allow for the dispersant to be directly sprayed on heavily oiled areas. Small vessel deployment of a single nozzle, high pressure/low flow system designed to deliver smaller quantities of dispersant over a significant spray swath width is quite useful for dispersant application to smaller spills. Single nozzle systems with a low pressure/high flow system are advantageous in that they allow easy variation of the output flow rate and droplet size settings. The ability to vary output flow rate is advantageous where a highly variable surface slick exists.

Single-point spray systems generate a spray pattern directed out from the side of a vessel without the need for an outrigger boom or spray arm system to support the nozzle. The system includes a pumping or pressure system to deliver dispersant to the nozzle, associated piping and valves, and appropriate meters and gauges, as well as a mixer, overboard suction and a strainer. A typical configuration can include one nozzle system each on the port and starboard sides. Dispersant can be applied either neat or diluted, depending on the estimated required dosage. For safety reasons, spraying should be with the wind, not into it.

15.5.5 Dispersant Application Vessels

It is desirable that vessels used for dispersant application should have the following characteristics:

- A carrying capacity that allows for storage of dispersant and fuel for two days of operations
- A large enough size to accommodate personnel, equipment, and dispersant
 - Vessels in the range of 20-50 ft (6-15 m) in length have been shown to be acceptable
- Large, open decks that allow access to the water surface
- A capability for high speed (>10-20 knots [18.5-37 km/hr]) in order to transit swiftly to oil spills and apply dispersant in the critical, early stages of the spill

15.5.6 Advantages and Disadvantages of Vessel Application Systems

Table 15.5 compares the advantages and disadvantages of the various vessel-based application platforms.

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Table 15.5 Comparison of Vessel Application Systems

Source: Motolenich-Salas and Clark, 2005, based on Major, et al, 1994; ITOPF, 1987; and S.L. Ross, 2000.

System	Advantages	Disadvantages
Spray Arm System, application of dilute dispersant	<ul style="list-style-type: none"> • Uniform dosage/spray across swath width if spray overlaps • Simple dosage control and dispersant distribution • Wide range of adjustment possible for vessel speed and dosage without changing nozzles 	<ul style="list-style-type: none"> • Heavy piping suspended over the side sensitive to sea state; complicated boom attachment/ship modification often required; boom contact with water possible on ship roll • Fine droplets easily blown off target due to wind • Loss of dispersant effectiveness due to dilution prior to application at low dispersant-to-oil ratio (DOR) • Limited spray location control • Limited spray speed due to bow wave created by ship pushing oil slick out of the way • Low treat rate due to slower speed and small swath width • Requires installation on vessel, not routinely available
Spray Arm System, application of neat dispersant	<ul style="list-style-type: none"> • Uniform dosage/spray across swath width • Most effective use of dispersant • Typically fewer passes/number of systems needed than dilute application to effectively apply dispersants 	<ul style="list-style-type: none"> • Heavy piping suspended over the side sensitive to sea state; complicated boom attachment/ship modification often required; boom contact with water possible on ship roll • Fine droplets easily blown off target due to wind • Limited spray location control • Limited spray speed due to bow wave created by ship pushing oil slick out of the way • Lower treatment rate due to slower speed and small swath width • Requires installation on vessel, not routinely available • Dispersant inventory can be rapidly exhausted
Fire Monitor System, application of dilute dispersant	<ul style="list-style-type: none"> • Widely available on larger vessels • A vessel with two monitors can cover up to 3-4 times the area of spray arm systems due to larger swath width and faster speeds • Droplets less sensitive to wind • Rugged; withstands permanent installation and better suited to rough weather/sea conditions • Can be permanently mounted without interfering with other operations • Can apply surface mixing after dispersant application • Spray can be directed to heavily oiled areas by an operator 	<ul style="list-style-type: none"> • Variations in dosage across swath width can lead to uneven coverage resulting in limited oil encounter rate • Requires attention to generate the appropriate dispersant droplet sizes for effective mixing with oil slicks • Possible loss of dispersant effectiveness due to dilution prior to application at low DOR • High water flow rates lead to high dispersant consumption, potential for wastage and over-application • Difficult to control dispersant dosage rates

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System	Advantages	Disadvantages
Single Nozzle System, application of neat dispersant	<ul style="list-style-type: none"> • Wider range of flow rates possible; high flows easily achieved • Wider swath widths than multi-nozzle spray arm systems • Simple installation, maintenance, and operation vs. spray arms • Spray can be directed to heavily oiled areas by an operator 	<ul style="list-style-type: none"> • Non-uniform spray along swath width • Droplet sizes may need to be larger than droplets from spray arm systems in high wind situations • Little experience with field use (technology still evolving) • Dispersant inventory can be rapidly exhausted • Higher risk of over-dosing

15.6 Weather Considerations

Dispersant application can be limited by severe weather conditions. Table 15.6 provides a rough description of the Beaufort Scale of wind force and Table 15.7 provides general guidelines on the limiting weather conditions for the various dispersant application systems. The ultimate decision with regard to safety and effectiveness under prevailing weather conditions is to be made by the owners and operators of the vessels and aircraft in consultation with the Incident Commander.

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Table 15.6 Beaufort Scale of Wind Force (Canadian Government Publishing Center, 1983)

Beaufort Number	Mean Wind Speed (Knots)	Descriptive Terms	Appearance of the Sea if the Fetch* and Duration of the Blow Have Been Sufficient to Develop the Sea Fully
0	0	Calm	Sea like a mirror.
1	2	Light Air	Ripples but without foam crests.
2	5	Light Breeze	Small wavelets; crests have a glassy appearance and do not break.
3	9	Gentle Breeze	Large wavelets; crests begin to break.
4	13	Moderate Breeze	Small waves, becoming longer; fairly frequent white "horses."
5	19	Fresh Breeze	Moderate waves; many white "horses." Chance of some spray.
6	24	Strong Breeze	Large waves begin to form; some spray.
7	30	Near Gale	Sea heaps up; white foam from breaking waves along the direction of the wind.
8	37	Gale	Moderately high waves of greater length; the foam is blown in well-marked streaks along the direction of the wind.
9	44	Strong Gale	High waves; dense streaks of foam along the direction of the wind.
10	52	Storm	Very high waves with long overhanging crests; great foam patches; visibility effects.
11	60	Violent Storm	Exceptionally high waves; visibility seriously affected.
12	68	Hurricane	The air is filled with foam and spray; sea completely white with driving spray; visibility very seriously affected.

* Distance traversed by waves without obstruction

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Table 15.7 Weather Limitations for Dispersant Application Systems

	Approximate Upper Limit on Weather and Sea State Conditions for Safe and Effective Spraying Operations		
Application System	Beaufort Scale	Wind Speed (Knots)	Significant Wave Height (ft)
Workboats (Tugboat Type)	3-5	7-21	1-9
Single-Engine Airplanes	5	17-21	6-9
Medium-Sized Helicopters	5-6	17-27	6-17
Small Multi-Engine Aircraft	5-6	17-27	6-17
Large Multi-Engine Aircraft	7	30-35	17-23

15.7 Checklists for Dispersant Application

Dispersant treatment of oil spills has been shown to be effective when the proper application system and procedures are used. Several factors must be considered before applying chemical dispersants. The checklists in Appendix E, page 190, may be helpful in advance planning of spraying operations.

In addition, some government agencies require that detailed information be supplied before permits can be issued for dispersant application. Even if dispersants have been pre-approved, such data may be required and its submission can cause significant delay in obtaining approval if the requested information is not readily available or familiar to the individual responsible for providing it. Appendix E also includes some of the information requests that have been experienced by ExxonMobil personnel in various drills.

16.0 ADDITIONAL NOTEWORTHY CASE STUDIES

Several case studies were discussed in section 8. This section summarizes additional noteworthy applications of dispersant during the past 15 years. Fortunately, the rate of major oil spills has dropped very significantly over the recent years (3.7 spills per year with releases over 700 tonnes during 2000-06 versus 25.2 per year during 1970-79 and about 8.5 per year during 1980-99) (ITOPF Handbook, 2007). However, there continue to be “opportunities” for dispersant deployment and government receptivity to its use continues to gradually improve.

16.1 *Braer, Scotland (Harris, 1995; Davies and Topping, 1997)*

During a severe storm, the tanker *Braer* grounded off the coast of Scotland in January 1993. The vessel broke up in three sections. A total of 84,700 tonnes of *Gulfaks* crude oil and about 1,500 tonnes of heavy bunker oil were released from the ship, i.e., essentially the entire cargo. A major portion of the oil was naturally dispersed due to the high wave energy and the dispersion characteristics of the *Gulfaks* crude oil. Due to severe weather, dispersant application was delayed until days 2 and 3 of the spill when dispersants were sprayed from DC-3 aircraft and by helicopter under marginally acceptable weather conditions. Approximately 120 tonnes of dispersant, including Dasic products, were sprayed on an estimated 2,000 tonnes of oil. Some of the dispersant blew onshore and missed the oil.

According to the Ecological Steering Group on the Oil Spill in Shetland, the impact of this spill was minimal except for a few offshore areas where high hydrocarbon levels were found in sediments that were deposited in deep water. On-shore vegetation areas impacted by dispersant spray recovered by the following growing season. This is the most studied spill in which most or all of the oil dispersed into the sea not far from shore and is the strongest evidence available that dispersing oil near shore can be accommodated by the marine environment without devastating effects. The studies carried out have been documented by the BBC in a video entitled “A Perfect Oil Spill.”

16.2 *Sea Empress, Wales (Lunel, et al, 1997)*

In February, 1996, the *Sea Empress* grounded at the entrance to Milford Haven, Wales. An estimated 65,300 tonnes of Forties Blend crude oil and 336 tonnes of heavy fuel oil were released. A total of 404 tonnes of dispersants were applied from DC3 and C-130 Hercules aircraft at a dispersant-to-oil ratio of 1:60. The dispersants Corexit[®] 9500, Dasic LTSW, Dasic Slickgone NS, Dispolene 34S, Enersperse 1583, Finasol OSR-51, and Superdispersant 25 were applied. Fluorometry confirmed the successful dispersion of oil even when visual signs of dispersion were absent. Overall, an estimated 50% of the spilled oil was naturally and/or chemically dispersed. There was clear value in having a dispersant operation in place as a first response. It was concluded that dispersant use probably prevented 57,000 to 110,000 tonnes of emulsified oil from impacting the shoreline.

16.3 *Captain Field, North Sea (Lewis, et al, 1998c)*

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Approximately 685 tonnes of crude oil were spilled from an FPSO (Floating Production Storage and Off-loading) vessel in the Captain field in August 1997. A 7.5% solution of Corexit[®] 9500 in seawater was applied by vessel. A mass balance calculation determined that 75% to 85% of the spilled oil was dispersed by Corexit 9500 initially applied from the vessel and 1% to 15% was dispersed by Corexit 9500 sprayed from aircraft. The mass balance calculation indicated successful dispersion despite a very low dispersant-to-oil ratio of 1:100.

16.4 High Island Pipeline System, Texas (Henry, 2005)

In January 1998, a leak developed in a pipeline belonging to High Island Pipeline in the Gulf of Mexico, approximately 100 km southeast of Galveston, Texas. The next day dispersant use was approved and carried out under the pre-approval authority for that area. Some 2000 barrels of oil were treated with 3000 gallons of Corexit 9527 via aircraft. Application was by a DC-4 and a DC-3. Both aerial surveillance and in-situ fluorometry monitoring confirmed that the overall operation was highly effective.

16.5 Pipeline Spill, Nigeria (Cutter Information Corp., 1998a; Lunel and Bailey, 1998)

A ruptured undersea pipeline resulted in the release of 5,700 tonnes of crude oil off the coast of Nigeria during January 1998. Corexit 9500 was applied from Twin Otter aircraft, helicopters, and vessels. Corexit 9500 was effective on emulsified crude oil even 12 days after the spill. Fluorometry measurements of subsurface oil concentrations showed that Corexit 9500 successfully dispersed the emulsified oil.

16.6 Red Seagull, Gulf of Mexico (Cutter Information Corp., 1998b; Henry, 2005)

Approximately 64 tonnes of Arabian light crude oil were released from the tanker *Red Seagull* off the coast of Texas in January 1998, reportedly due to a missing hold plug. A fire monitor was used to spray about 303 liters of Corexit 9500 applied at 6% and 3% solutions. Fluorometry measurements indicated that the dispersant treatment was successful. The significance of this response was the demonstration that a fire monitor could be modified and used as an emergency dispersant application system for small spills.

16.7 Other Pipeline Spills, Gulf of Mexico (Cutter Information Corp., 1998b and c., 2000; Henry, 2005)

1998: In October, a pipeline spill occurred in the Gulf of Mexico, at Mississippi Canyon, releasing over 580 tonnes (3700 bbls) of crude oil. The spill occurred in an area where dispersant use was pre-approved and, in less than 8 hours after the spill was reported, dispersant was applied to the slick. Dispersant was applied on isolated patches of oil the following day. Altogether, DC-3 and DC-4 aircraft applied an estimated 4900 gallons (18,500 liters) of Corexit 9527 and Corexit 9500. By the third day, no large slicks were reportedly present. According to the US Coast Guard, dispersant application prevented the oil from stranding on an area of the coast which contained bird sanctuaries.

2000: Over 300 tonnes of unidentified crude oil spilled from the Poseidon pipeline reportedly after an anchor was accidentally dropped on it in January. Almost complete dispersion was

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achieved by application of 20 tonnes of Corexit 9527 at a dispersant-to-oil ratio of 1:15 using DC-3 and DC-4 aircraft. The dispersant applications were successful in breaking up the oil and accelerating degradation. Aerial observations indicated that only small patches of sheen remained.

2004: When Hurricane Ivan passed through the Mississippi delta in the Gulf of Mexico in September, it completely severed two major pipelines, destroyed storage tanks and damaged platforms. Over the following 20 days, approximately 7000 barrels (1100 tonnes) of light crude oil were released near two major wildlife refuges. Because the spill was in shallow water outside the pre-authorized zone, dispersants were approved only as a tactical response, targeting oil that escaped the primary recovery operations and presented a direct risk to wildlife and estuarine habitats. Overall, some 350 gallons of Corexit 9527 were applied by fire monitor and 5000 gallons of Corexit 9500 were applied via five DC-3 sorties. Dispersant effectiveness seemed to vary with the amount of energy present in the water. This was the first use of dispersant in shallow waters in the US since passage of the Oil Pollution Act of 1990. There were no reports of damage to the sensitive habitats.

16.8 *Tasman Spirit*; Karachi, Pakistan (Saeed and Rizvi, 2005)

The oil tanker *Tasman Spirit* grounded near shore in a channel of the port of Karachi, Pakistan in July, 2003, eventually spilling nearly 30,000 tonnes of crude oil. The environment in which the spill occurred is a rich and diverse tropical marine/estuarine ecosystem that includes extensive mangrove forests, 50 species of birds, sea turtle habitats, dolphins, porpoises, whales, lizards, etc. Part of the response included dispersant spraying by air; however, the response capability reportedly was limited. The impact was extensive contamination of an area of 40 square kilometers and a coastline of 7.5 km. Over 700 hectares of mangroves were oiled and seedling loss was estimated at over 50 million seedlings. Some 300,000 people were affected by the 12,000 tonnes of evaporated oil, thought to be the largest population exposure from a spill in history. Full recovery of the area is expected to take 5-10 years.

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17.0 REFERENCES AND BIBLIOGRAPHY

Allen, A.A. 1988. "Comparison of Response Options for Offshore Oil Spills." **Proc. 11th Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

API (American Petroleum Institute). 1999a. "Fate of Spilled Oil in Marine Waters: Where Does It Go?, What Does it Do? How Do Dispersants Affect It?" **API Publication No. 4691**. Washington, D.C.

API (American Petroleum Institute). 1999b "A Decision-Maker's Guide to Dispersants. A Review of the Theory and Operational Requirements." **API Publication No. 4692**. Washington, D.C.

ASTM. 1977. **Chemical Dispersants for the Control of Oil Spills**. ASTM Special Technical Publication 659. ASTM, West Conshohocken, Pennsylvania.

ASTM International. 2007. **ASTM Standards on Hazardous Substances and Oil Spill Response**. 2007 Edition. West Conshohocken, Pennsylvania.

Aurand, D., G. Coelho, J. Clark, and G. Bragin. 1999. "Goals, Objectives and Design of a Mesocosm Experiment on the Environmental Consequences of Nearshore Dispersant Use." **Proc. 22nd Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

AURIS (Aberdeen University Research and Industrial Services, LTD). 1994. **Scientific Criteria to Optimize Oil Spill Clean-Up Operations and Effort**. AURIS Environmental, Aberdeen, Scotland.

AURIS. 1995. **Scoping Evaluation of the Biological Recovery of Mangroves, Coral Reefs, Sea Grasses and Sedimentary Shores**. AURIS Environmental, Aberdeen, Scotland.

Baca, B., G. Ward, C. Lane, and P. Schuler. 2005. "Net Environmental Benefit Analysis (NEBA) of Dispersed Oil on Nearshore Tropical Ecosystems Derived from the 20 Year 'TROPICS' Field Study." **Proc. of 2005 International Oil Spill Conference**. American Petroleum Institute. Washington, DC.

Baker, J. 1995. "Net Environmental Benefit Analysis for Oil Spill Response." **Proc. of 1995 International Oil Spill Conference**. American Petroleum Institute. Washington, DC.

Baker, K. 2003. "Understanding Paraffin and Asphaltene Problems in Oil and Gas Wells." **Petroleum Technology Transfer Council**. Available at http://www.pttc.org/solutions/sol_2003/523.htm.

ExxonMobil Oil Spill Dispersant Guidelines

Ballou, T. G., S. C. Hess, R. E. Dodge, A. H. Knap, and T. D. Sleeter. 1989. "Effects of Untreated and Chemically Dispersed Oil on Tropical Marine Communities: A Long-Term Field Experiment." **Proc. 1989 International Oil Spill Conference**, San Antonio, Texas.

Becker, K. W., L. G. Coker and M. A. Walsh. 1991 "A Method For Evaluating Oil Spill Dispersants. Exxon Dispersant Effectiveness Test (EXDET)." **Oceans '91 Conference Proceedings**, Oceanic Engineering Society of IEEE. Honolulu, Hawaii.

Belore, R. and S. Ross. 1999. "Testing and Development of a Single-Nozzle Spray System for Vessel-Based Dispersant Delivery." **Proc. 22nd Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

Belore, R. 2002. "Wave Tank Tests to Determine the Effectiveness of Corexit 9500 Dispersant on Hibernia Crude Oil Under Cold Water Conditions." **Proc. 25th Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

Belore, R. 2003. "Large Wave Tank Dispersant Effectiveness Testing in Cold Water." **Proc. 2003 International Oil Spill Conference**, API. Washington, DC

Betton, C.I. 1994. "Oils and Hydrocarbons." **Handbook of Ecotoxicology**. Vol. II. P. Calow, ed. Blackwell Scientific Publications, Boston, Massachusetts.

Blackall, P. J. and G. A. Sergy. 1983. "The BIOS Project—an Update." **Proc. 1983 International Oil Spill Conference**, San Antonio, Texas.

Blondina, G. J., M. M. Singer, I. Lee, M. T. Ouano, R. S. Tjeerdema, and M. L. Sowby. 1999. "Influence of Salinity on Petroleum Accommodation by Dispersants." **Spill Science and Technology Bulletin 5**.

Blondina, G. J., M. L. Sowby, M. T. Ouano, M. M. Singer and R. S. Tjeerdema. 1997. "Comparative Efficacy of Two Corexit Dispersants as Measured Using California's Modified Swirling Flask Test." **Proc. 20th Arctic and Marine Oil Spill Program Technical Seminar**. Vancouver, Canada.

Bocard, C., G. Castaing, and C. Gatellier. 1984. "Chemical Oil Dispersion in Trials at Sea and in Laboratory Tests: the Key Role of Dilution Processes." **Oil Spill Chemical Dispersants, Research, Experience, and Recommendations**. ASTM STP 840. T. E. Allen, ed. American Society for Testing and Materials. Philadelphia, Pennsylvania.

Bragin, G., G. Coelho, E. Febbo, J. Clark, and D. Aurand. 1999. "Coastal Oil Spill Simulation System Comparison of Oil and Chemically Dispersed Oil Released in Near-shore Environments: Biological Effects." **Proc. 22nd Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

ExxonMobil Oil Spill Dispersant Guidelines

Brown, H.M., and R.H. Goodman. 1996. "The Use of Dispersants in Broken Ice." **Proc. 19th Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

Byford, D.C. 1982. "The Development of Dispersants for Application at Low Temperatures." **Proc. 5th Arctic and Marine Oil Spill Program Technical Seminar**. Edmonton, Canada.

Canadian Government Publishing Center, 1983. **Wind and Sea**. Ottawa, Canada.

Canevari, G.P. 1971. "Oil Spill Dispersants: Current Status and Future Outlook." **Proc. of Joint Conference on Prevention and Control of Oil Spills**. API, Washington, DC.

Canevari, G.P. 1973. "Development of the Next Generation Chemical Dispersants." **Proc. of Joint Conference on Prevention and Control of Oil Spills**. API, Washington, DC.

Canevari, G. P. 1979. "The Restoration of Oiled Shorelines by the Proper Use of Chemical Dispersants." **Proc. 1979 International Oil Spill Conference**. API. Washington, DC.

Canevari, G.P., and R.J. Fiocco. 1997. "Crude Oil Vanadium and Nickel Content Can Predict Emulsification Tendency." **Proc. 1997 International Oil Spill Conference**. API. Washington, DC.

CEPRECO. 2006. **Recommendations About the Cleaning of the Coast of Lebanon Due to the Oil Spill After the Bombing Attack of Jiyeh Power Plant**, Ministry of Presidency. Spain.

Chen, A. C. T. 1999. "Design Considerations for a Fire-Monitor Based Dispersant Application System." **Proc. 22nd Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

Clayton, J. R. Jr., J. R. Payne, and J. S. Farlow. 1993. **Oil Spill Dispersants. Mechanisms of Action and Laboratory Tests**. CRC Press, Inc. Boca Raton, Florida. 113 pp.

CONCAWE. 1988. **A Field Guide to the Application of Dispersants to Oil Spills**. Report No. 2/88. Den Haag, Netherlands.

Cox, J.C., and L.A. Schultz. 1981. "Dispersant Effectiveness Under Arctic Conditions, Including Ice." **Proc. 4th Arctic and Marine Oil Spill Program Technical Seminar**. Edmonton, Canada.

Cutter Information Corporation. 1986. **Oil Spill Intelligence Report** Vol. IX, No. 29. Arlington, Massachusetts.

Cutter Information Corporation. 1998a. **Oil Spill Intelligence Report** Vol. XXI, Nos. 3 and 4. Arlington, Massachusetts

ExxonMobil Oil Spill Dispersant Guidelines

Cutter Information Corporation. 1998b. **Oil Spill Intelligence Report** Vol. XXI, No. 5. Arlington, Massachusetts.

Cutter Information Corporation. 1998c. **Oil Spill Intelligence Report** Vol. XXI, No. 39. Arlington, Massachusetts.

Cutter Information Corporation. 1999c. **Oil Spill Intelligence Report** Vol. XXII, No. 36. Arlington, Massachusetts.

Cutter Information Corporation. 2000. **Oil Spill Intelligence Report**, Vol. XXIII, No. 4. Arlington, Massachusetts.

Cutter Information Corporation. 2000. **International Oil Spill Statistics: 1999**. Arlington, MA.

Daling, P. S. and T. Strom. 1999. "Weathering of Oils at Sea: Model/Field Data Comparisons." **Spill Science and Technology Bulletin** 5:63-74.

Daling, P. S., O. M. Aamo, A. Lewis and T. Strom-Kristiansen. 1997. "SINTEF/IKU Oil Weathering Model: Predicting Oils' Properties at Sea." **Proc. 1997 International Oil Spill Conference**, API. Washington, DC.

Davidson, A. 1990. **In the Wake of the Exxon Valdez**. Sierra Club Books. San Francisco, California.

Davies, J. M. and G. Topping, eds. 1997. **The Impact of an Oil Spill in Turbulent Waters: The Braer**. The Stationary Office Ltd., Edinburgh, Scotland. 263 pp.

Desmarquest, J. P., J. Croquette, F. Merlin, C. Bocard, G. Castaing, and C. Gatellier. 1985. "Recent Advances in Dispersant Effectiveness Evaluation." **Proc. 1985 Oil Spill Conference**, API. Washington, DC.

Dicks, B., T. Moller, and R. Santner. 1998. "The *Evoikos* and *Pontoon 300* Incidents – a Technical Advisors' Perspective." Available at http://www.itopf.org/paj_98.pdf#search=%22evoikos%20and%20pontoon%20300%22.

Dodge, R.E., B.J. Baca, A.H. Knap, S.C. Snedaker, and T.D. Sleeter. 1995. "The Effects of Oil and Chemically Dispersed Oil in Tropical Ecosystems: 10 Years of Monitoring Experimental Sites." **MSRC Technical Report 95-014**. Marine Spill Response Corporation. Herndon, VA.

ExxonMobil Oil Spill Dispersant Guidelines

Ebert, T.A., R. Downer, J.R. Clark, and C.A. Huber. 2008. "Summary of Studies of Corexit Dispersant Droplet Impact Behavior Into Oil Slicks and Dispersant Droplet Evaporation." **Proc. of the 2008 International Oil Spill Conference**, API. Washington, DC.

Etkin, D. S. 1999. **Oil Spill Dispersants: from Technology to Policy**. Cutter Information Corp. Arlington, Massachusetts; 306 pp.

Exxon Mobil Corp. 1985. **Oil Spill Cleanup Manual. Volume III Chemical Dispersants**.

ExxonMobil Research and Engineering Company. 2005. **ExxonMobil Oil Spill Response Field Manual**; Fairfax, Virginia.

Fingas, M.F. 2007. "Estimation of Oil Spill Behavior Parameters from Readily-Available Oil Properties." **Proc. 30th Arctic and Marine Oil Spill Program Technical Seminar**. Edmonton, Canada.

Fingas, M.F., B. Fieldhouse, J. Lane, and J.V. Mullin. 2001. "What Causes the Formation of Water-in-Oil Emulsions?" **Proc. of the 2001 International Oil Spill Conference**. API. Washington, DC.

Fingas, M. F, K. A. Hughes, and M. A. Schweitzer. 1987. "Dispersant Testing at the Environmental Emergencies Technology Division." **Proc. 10th Arctic and Marine Oil Spill Program Technical Seminar**. Alberta, Canada.

Fingas, M. F., D. A. Kyle, N. D. Laroche, B. G. Fieldhouse, G. Sergy, and R. G. Stoodley. 1995. "The Effectiveness of Spill Treating Agents." **The Use of Chemicals in Oil Spill Response**, ASTM STP1252, P. Lane, ed. ASTM, Philadelphia, Pennsylvania.

Fingas, M. F., R. G. Stoodley, N. Stone, R. Hollins, and I. Bier. 1991. "Testing the Effectiveness of Spill-Treating Agents: Laboratory Test Development and Initial Results." **Proc. 1991 International Oil Spill Conference**. API. Washington, DC.

Fiocco, R. J. and A. Lewis. 1999. "Oil Spill Dispersants." **Journal International Union of Pure and Applied Chemistry** 71:27-42.

Fiocco, R. J., P.S. Daling, G. DeMarco and R.R. Lessard. 1999a. "Advancing Laboratory/Field Dispersant Effectiveness Testing." **Proc. 1999 International Oil Spill Conference**, API. Washington, D.C.

ExxonMobil Oil Spill Dispersant Guidelines

Fiocco, R. J., P.S. Daling, G. DeMarco, R.R. Lessard and G.P. Canevari. 1999b. "Chemical Dispersibility of Heavy Bunker Fuel Oil." **Proc. 22nd Arctic Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

Fiocco, R. J. and R.R. Lessard. 1997. "Demulsifying Dispersant for an Extended Window of Use." **Proc. 1997 International Oil Spill Conference**, API. Washington, DC.

Fiocco, R.J., R.R. Lessard, G.P. Canevari, K.W. Becker and P.S. Daling. 1995. "The Impact of Oil Dispersant Solvent on Performance." **The Use of Chemicals in Oil Spill Response**, ASTM STP 1252, P. Lane, ed. ASTM, Philadelphia, Pennsylvania.

Fuller, C., J. Bonner, T. McDonald, C. Page, G. Bragin, J. Clark, D. Aurand, A. Hernandez, and A. Ernest. 1999. "Comparative Toxicity of Simulated Beach Sediments Impacted With Both Whole and Chemical Dispersions of Weathered Arabian Medium Crude Oil." **Proc. 22nd Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

George-Ares, A. and J. R. Clark. 2000. "Aquatic Toxicity of Two Corexit[®] Dispersants." **Chemosphere** 40:897-906.

George-Ares, A. and J. R. Clark. 1997. "Acute Aquatic Toxicity of Three Corexit Products: An Overview." **Proc. 1997 International Oil Spill Conference**, API. Washington, DC.

Getter, C. D. and T. G. Ballou. 1985. "Field Experiments on the Effects of Oil and Dispersants on Mangroves." **Proc. 1985 International Oil Spill Conference**. API. Washington, DC.

Giammona, C., K. Binkley, R. Fay, G. Denoux, M. Champ, R. Geyer, F. Bouse, I. Kirk, D. Gardisser, and R. Jamail. 1994. **Aerial Dispersant Application: Field Testing Research Program Alpine, Texas**. Marine Spill Response Corporation, Technical Report Series 94-019. Herndon, Virginia.

Gilfillan, E. S., S. A. Hanson, D. Vallas, R. Gerber, D. S. Page, J. Foster, J. Hotham, and S. D. Pratt. 1983. "Effect of Spills of Dispersed and Non-Dispersed Oil in Intertidal Infaunal Community Structure." **Proc. 1983 International Oil Spill Conference**, API. Washington, DC.

Guyomarch, J., O. Kerfourn, and F.X. Merlin. 1999. "Dispersants and Demulsifiers: Studies in the Laboratory, Harbor and Polludrome." **Proc. 1999 International Oil Spill Conference**, API. Washington, DC.

Guyomarch, J. and F.X. Merlin. 1999. "Study of the Feasibility of Chemical Dispersion of Viscous Oils & Water-in-Oil Emulsions." **Proc. of the 22nd Arctic and Marine Oilspill Program (AMOP) Technical Seminar**. Calgary, Canada.

ExxonMobil Oil Spill Dispersant Guidelines

Harris, C. 1995. “The *Braer* Incident: Shetland Islands, January 1993.” **Proc. 1995 International Oil Spill Conference**, API. Washington, DC.

Harris, C. 1997. “The *Sea Empress* Incident: Overview and Response at Sea.” **Proc. 1997 International Oil Spill Conference**, API. Washington, DC.

Henry, C. 2005. “Review of Dispersant use in US Gulf of Mexico Waters Since the Oil Pollution Act of 1990.” **Proc. 2005 International Oil Spill Conference**, API. Washington, DC.

Henry, C. B., P. O. Roberts, and E. B. Overton. 1999. “A Primer on In Situ Fluorometry to Monitor Dispersed Oil.” **Proc. 1999 International Oil Spill Conference**, API. Washington, DC.

Huber, C.A. 2006. Personal communication based on analysis of recent land-based air application tests.

IMO/UNEP (International Maritime Organization and United Nations Environment Programme). 1995. **IMO/UNEP Guidelines on Oil Spill Dispersant Application Including Environmental Considerations**. IMO. London, UK. 55 pp.

IOPC Fund. 2006. “*Prestige*; Spain 13th November 2002.” Available from <http://www.iopcfund.org/prestige.htm>.

IPIECA. 1993. “Dispersants and Their Role in Oil Spill Response.” **The IPIECA Report Collection**. Volume 5. London, UK.

IPIECA. 2000. “Guidelines on Biological Impacts of Oil Pollution.” **The IPIECA Report Collection** 2nd ed. Volume 1. London, UK.

IPIECA. 2000. “Choosing Spill Response Options to Minimize Damage. Net Environmental Benefit Analysis.” **The IPIECA Report Collection**. Volume 10. London, UK.

ITOPF (International Tanker Owners Pollution Federation Ltd.). 1987. **Response to Marine Oil Spills**. Witherby and Co. Ltd. London, UK.

ITOPF. 2004. “*Prestige* (Spain 2002).” Available from <http://www.itopf.com/casehistories.html#prestige>.

ITOPF. 2005. **Technical Information Paper 4: The Use of Chemical Dispersant to Treat Oil Spills**. ITOPF, London, UK.

ITOPF. 2007. **ITOPF Handbook**. London, UK.

ExxonMobil Oil Spill Dispersant Guidelines

Johanson, G., and A. Boman. 1991. "Percutaneous Absorption of 2-Butoxyethanol Vapour in Human Subjects." **British Journal of Industrial Medicine**. Vol 48; 788-792.

Lessard, R.R. and G. DeMarco. 2000. "The Significance of Oil Spill Dispersants." **Spill Science and Technology Bulletin**. Vol. 6. No.1.

Lessard, R.R., DeMarco, G., R.J. Fiocco, T. Lunel and A. Lewis. 1998. "Recent Advances in Oil Spill Dispersant Technology with Emphasis on New Capability to Disperse Heavy Oil." **Society of Petroleum Engineers International Conference**. Caracas, Venezuela. SPE 46405.

Lewis, A., 2003. UK 2003 Oil Spill Dispersant Sea Trials; Overview of Work Done and Results Achieved. Unpublished work.

Lewis, A. and D. Aurand. 1997. "Putting Dispersants to Work: Overcoming Obstacles." **API Publication No. 4652A**. Washington, D. C.

Lewis, A., A. Crosbie, L. Davies and T. Lunel. 1998a. "Dispersion of Emulsified Oil at Sea." **Report AEAT-3475**. National Environmental Technology Centre, AEA Technology. Oxfordshire, United Kingdom. 288 pp.

Lewis, A., A. Crosbie, L. Davies and T. Lunel. 1998b. "Large Scale Field Experiments into Oil Weathering at Sea and Aerial Application of Dispersants." **Proc. 21st Arctic and Marine Oil Spill Program Technical Seminar**. Edmonton, Canada.

Lewis, A., A. Crosbie and N. Bailey. 1998c. "Dispersion of Spilled Captain Crude Oil." National Environmental Technology Centre. **Report No. AEAT-2755 Issue 2**. AEA Technology, Oxfordshire, United Kingdom.

Lewis, A., P. Daling, T. Strom-Kristiansen, A. Nordvik and R. Fiocco. 1995. "Weathering and Chemical Dispersion of Oil at Sea." **Proc. 1995 International Oil Spill Conference**. API. Washington, DC.

Lindblom, G.P. 1979. "Logistic Planning for Oil Spill Chemical Use." **Proc. 1979 International Oil Spill Conference**. API. Washington, DC.

Lindblom, G.P. and B.S. Cashion. 1983. "Operational Considerations for Optimal Deposition Efficiency in Aerial Application of Dispersants." **Proc. 1983 International Oil Spill Conference**. API. Washington, DC.

Lunel, T. 1995. "The Braer Spill: Oil Fate Governed by Dispersion." **Proc. 1995 International Oil Spill Conference**, API. Washington, DC.

ExxonMobil Oil Spill Dispersant Guidelines

Lunel, T. and N. Bailey. 1998. "In Situ Monitoring at the Idoho Pipeline Spill, Nigeria." **Report AEA/WMES/205113001**. National Environmental Technology Centre, AEA Technology. Oxfordshire, UK.

Lunel, T., J. Rusin, N. Bailey, C. Halliwell and L. Davies, 1997. "The Net Environmental Benefit of a Successful Dispersant Operation at the *Sea Empress* Incident." **Proc. 1997 International Oil Spill Conference**. API. Washington, DC.

Lunel, T., R. Swannell, P. Wood, J. Rusin, N. Bailey, C. Halliwell, L. Davies, M. Sommerville, A. Dobie, D. Mitchell, M. McDonagh and K. Lee. 1996. "Shoreline Clean Up During the *Sea Empress* Incident: The Role of the Surf Washing (Clay-Oil Flocculation), Dispersants and Bioremediation." **Proc. of the 19th Arctic and Marine Oilspill Program Technical Seminar**. Calgary, Canada.

Mackay, D. 1995. "Effectiveness of Chemical Dispersants Under Breaking Wave Conditions." **The Use of Chemicals in Oil Spill Response**, ASTM STP 1252, P. Lane, ed., ASTM, Philadelphia, Pennsylvania.

Mackay, D. and F. Szeto. 1981. "The Laboratory Determination of Dispersant Effectiveness Method and Results." **Proc. 1981 International Oil Spill Conference**. API. Washington, DC.

Mackin, J. G. 1970. "A Study of the Effect of an Oil Dispersal Agent Corexit in an Oil Cleanup Operation." Texas A&M University. College Station, Texas. 30 pp.

Martinelli, F. N. 1984. "The Status of Warren Spring Laboratory's Rolling Flask Test." **Oil Spill Chemical Dispersants, Research, Experience, and Recommendations**. ASTM STP 840. T. E. Allen, ed. American Society for Testing and Materials. Philadelphia, Pennsylvania.

MAFF (Ministry of Agriculture, Fisheries and Food). 1994. **Review of Dispersant Use in the UK**. Burnham-on-Crouch, Essex, UK.

McAuliffe, C. D. 1989. "The Use of Chemical Dispersants to Control Oil Spills in Shallow Nearshore Waters." **Oil Dispersants: New Ecological Approaches**. ASTM STP 1018. L. Michael Flaherty, ed. ASTM. Philadelphia, Pennsylvania.

McAuliffe, C. D. 1991. **EPA Dispersant Effectiveness Workshop**. Edison, New Jersey.

Motolenich-Salas, K. and J. Clark. 2005. "Vessel Dispersant Application in Oil Spill Response: Research Review." **Proc. 2005 International Oil Spill Conference**. API. Washington, DC.

National Response Corporation. 1999. "NRC Commissions Dispersant Vessels." *Gulf Update*. 3 (2):1.

ExxonMobil Oil Spill Dispersant Guidelines

Nichols, J. A. and H.D. Parker. 1985. "Dispersants: Comparison of Laboratory Tests and Field Trials with Practical Experience at Spills." **Proc. 1985 International Oil Spill Conference**. API. Washington DC.

NOAA. 1990. **Excavation and Rock Washing Treatment Technology: Net Environmental Benefit Analysis**. NOAA. Seattle, WA.

NOAA (National Oceanic and Atmospheric Administration). 1998. **Dispersant Application Observer Job Aid**. Seattle, WA. 24 pp.

NRC (US National Research Council). 1989. **Using Oil Spill Dispersants on the Sea**. National Academy Press, Washington, DC. 335 pp.

NRC. 2003. **Oil in the Sea III. Inputs, Fates, and Effects**. National Academy of Sciences. Washington, DC.

NRC. 2005. **Oil Spill Dispersants. Efficacy and Effects**. National Academy of Sciences. Washington, DC.

Owens, E. H., C. R. Foget and W. Robson. 1984. "Experimental Use of Dispersants for Spill Countermeasures on Arctic Beaches." **Oil Spill Chemical Dispersants: Research, Experience, and Recommendations**. ASTM STP 840. T. E. Allen, ed. ASTM. Philadelphia, Pennsylvania.

Pace, C. B., J. R. Clark and G. E. Bragin. 1995. "Comparing Crude Oil Toxicity Under Standard and Environmentally Realistic Exposures." **Proc. of the 1995 International Oil Spill Conference**. API, Washington, DC.

Page, C., P. Sumner, R. Autenrieth, J. Bonner and T. McDonald. 1999. "Materials Balance on a Chemically-Dispersed Oil and a Whole Oil Exposed to an Experimental Beach Front." **Proc. 22nd Arctic and Marine Oil Spill Program Technical Seminar**. Calgary, Canada.

Pauwels, S. J. and J. R. Clark. 1993. "Overview of International Oil Spill Dispersant Toxicity Testing Requirements." **Proc. 1993 International Oil Spill Conference**, API. Washington, DC.

Pezeshki, S. R., R. D. DeLaune, J. A. Nyman, R. R. Lessard and G. P. Canevari. 1995. "Removing Oil and Saving Oiled Marsh Grass Using a Shoreline Cleaner." **Proc. 1995 International Oil Spill Conference**. API. Washington, DC.

Rice, S.D. 1973. "Toxicity and Avoidance Tests With Prudhoe Bay Crude Oil and Pink Salmon Fry." **Proc. 1973 International Oil Spill Conference**, API. Washington, DC.

ExxonMobil Oil Spill Dispersant Guidelines

Robbins, M.L., R. Varadaraj, J. Bock and S.J. Pace. 1995. "Effect of Stokes' Law Settling on Measuring Oil Dispersion Effectiveness." **Proc. 1995 International Oil Spill Conference**, API. Washington, DC.

Ross, S.L. 2000. "Laboratory Study to Compare the Relative Effectiveness of Corexit 9500 and 9527 on Viscous Oils." Report for ExxonMobil. Ottawa, ON, Canada.

Ross, S.L. 2004. **World Catalog of Oil Spill Response Products**, S. Potter, ed. The Lowe-Martin Group. Ottawa, Ontario.

Ross, S.L., R. Belore and K. Trudel. 2001. "Vessel-Based Dispersant Application: New Approaches, Equipment, and Logistics." **Proc. 2001 International Oil Spill Conference**, API. Washington, DC.

Ross, S.L., Lewis Oil Spill Consultancy, and MAR Inc. 2005. "Dispersant Effectiveness Tests: Relating Results from OHMSETT to At-Sea Rests." **Report prepared for US Dept. of the Interior Minerals Management Service**. Ottawa, ON Canada..

Ross, S.L. and MAR Inc. 2006. "Dispersant Effectiveness Testing on Viscous, U.S. Outer Continental Shelf Crude Oils." **Report for the US Dept. of the Interior Minerals Management Service**. Ottawa, ON, Canada.

Saeed, M.I. and S.H.N. Rizvi. 2005. "Natural Resource Damage Assessment Programme for *Tasman Spirit* Oil Spill in Pakistan." **Proc. 2005 International Oil Spill Conference**, API. Washington, DC.

SEA (Scientific and Environmental Associates, Inc.), ed. 1995. **Workshop Proc.: The Use of Chemical Countermeasure Product Data for Oil Spill Planning and Response**, Vol. 1, April 4-6, 1995. Leesburg, Virginia. 83 pp.

Sell, D., L. Conway, T. Clark, G.B. Picken, J. Baker, G.M. Dunnet, A.D. McIntyre and R. B. Clark. 1995. "Scientific Criteria to Optimize Oil Spill Cleanup." **1995 International Oil Spill Conference**. API. Washington, DC.

Sergy, G.A. 1985. "The Baffin Island Oil Spill (BIOS) Project: a Summary." **1985 International Oil Spill Conference**. API. Washington, DC.

Singer, M. M., D. L. Smalheer and R. S. Tjeerdema. 1990. "A Simple Continuous-Flow Toxicity Test System for Microscopic Life Stages of Aquatic Organisms." **Water Research** 24: 899-903.

Steen, A., and A. Findlay. 2008. "Frequency of Dispersant Use Worldwide." **Proc. 2008 International Oil Spill Conference**. API. Washington, DC.

ExxonMobil Oil Spill Dispersant Guidelines

Strøm-Kristiansen, T., A. Lewis, P.S. Daling, J.N. Hokstad and I. Singaas. 1997. "Weathering and Dispersion of Naphthenic, Asphaltenic, and Waxy Crude Oils." **Proc. 1997 International Oil Spill Conference**. API. Washington, DC.

Suidan, M. T. and Sorial, G. A., 2005. "Analysis of Dispersant Effectiveness of Heavy Fuel Oils and Weathered Crude Oils at Two Different Temperatures Using the Baffled Flask." University of Cincinnati, Department of Civil and Environmental Engineering, Cincinnati, Ohio.

Teas, H.J., R.R. Lessard, G.P. Canevari, C.D. Brown and R. Glenn. 1993. "Saving Oiled Mangroves Using a New Non-Dispersing Shoreline Cleaner." **Proc. 1993 International Oil Spill Conference**. API. Washington, DC.

Trudel, B.K., R. Belore, A. Lewis, A. Guarino and J. Mullin. 2005. "Determining the Viscosity Limits for Effective Chemical Dispersion: Relating OHMSETT Results to Those from Tests At-Sea." **Proc. 2005 International Oil Spill Conference**. API. Washington, DC.

USEPA (U. S. Environmental Protection Agency Oil Program Center). May 1999. **National Contingency Plan Product Schedule**. EPA. Washington, DC.

Weber, D.D., D.J. Maynard, W.D. Grondlund, and V. Konchin. 1981. "Avoidance Reactions of Migrating Adult Salmon to Petroleum Hydrocarbons." **Canadian Journal of Fish and Aquatic Science**. Vol. 38.

Wilson, D. and F. A. Putnam. 1982. **Surface Chemical Aspects of Oil Spill Sedimentation**. Massachusetts Institute of Technology. Report to the American Petroleum Institute. 92 pp.

Yeager, J.G. and Assoc. 1985. "US Crude and Products Imported." Prepared for the API. Washington, DC.

ZoBell, C.E. 1963. **International Journal of Air and Water Pollution**. Pergamon Press, New York.

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Appendix A Unit Conversions for Oil Spill Response

Volume

1 U.S. gallon = 231 in³ = 0.1337 ft³
1 barrel(s) (bbl) = 42 U.S. gallons = 5.615 ft³
1 bbl = 158.97 Liter (L) = 0.159 m³
1 U.S. gallon = 3.785 L
1 L = 0.26 gal
1 tonne of oil = 1,000 L = 1 m³ = about 264
gallons at a density of 1.0 g/ml
1 m³ = 6.29 bbl = 264.2 gal
1 ft³ = 0.0283 m³ = 7.48 gal
1 m³ = 10⁶ cm³ = 10³ L
Imperial gallon = 1.2 U.S. gallons
1 U.S. gallon = 0.83 Imperial. gallons

Volume Rate

L/hr x 0.0063 = bbl /hr
L/hr x 0.0044 = gpm
tonnes/hr (or m³/hr) x 4.4 = gpm
tonnes/hr x 6.3 = bbl /hr
bbl /hr x 0.7 = gpm
L/sec x 15.9 = gpm
gpm x 34.29 = bbl /day
m³/hr x 16.7 = L/min
L/min x 0.06 = m³/hr
gpm x 3.78 = L/min
bbl/day x 0.11 = L/min
bbl /day x 0.0292 = gpm

Area

Length

1 inch = 2.54 cm
1 foot = 30.38 cm
1 foot = 0.3048 m
1 meter = 3.2808 feet
1 statute mile = 0.87 nautical mile
1 mile = 1610 m = 5280 ft
1 nautical mile = 6076 feet
1 kilometer = 0.54 nautical miles (nm)
1 nautical mile = 1.852 km = 1852 m
1 nautical mile = 1.15 Statute miles
1 micron = m x 10⁻⁶ = mm x 10⁻³
1 fathom (6 ft) = 1.829 m
1 meter = 0.547 fathoms

Distance Rate

1 knot = 1.69 ft/sec
1 knot = 1.94 m/sec = 1.13 miles/hr
ft/sec x 0.593 = knots
m/sec x 1.94 = knots (about 2 x)
mph x 1.5 = ft/sec
knots x 51.4 = cm/sec

Weight

1 pound = 0.45 kilograms
1 kilogram = 2.2 pounds
lb/ft x 1.48 = kg/m
kg/m x 0.672 = pounds/ft
1 metric ton = 1,000 kg
(approximately = 1 long ton)

Pressure

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1 hectare = 10,000 m² (a 100 m square)
1 acre = 43,560 ft² = 0.4047 hectares = 247 km²
1 acre = 4,047 m²
1 hectare = 2.471 acres = 0.00386 sq miles
1 ft² = 0.0929 m²
1 mile² = 2.59 km²
1 square nautical mile (nm²) = 847 acres

1 pascal = 1 newton/m²
psi x 6.895 x 10³ = pascals
kg/m² x 0.206 = lb/ft²
1 bar = 14.7 psi = 100 kilo pascals = 10⁵ pascals
psi x 0.068 = bar

Area Application

gallons/acre x 9.35 = L/hectare
gallons/acre = liter/km² x 1.07 x 10⁻³
L/m² = thickness in mm
area (ft²) x thickness (inches) x 0.623 = volume (gallons)

Recovery Capacity in M³/Hr

W = sweep width, meters
V = sweeping speed, knots
T = oil layer thickness, mm

Capacity = W x V x T x 1.852 (m³/hr)

Oil Volume/Area

area (nm²) x slick thickness (mm) x 21,570 = oil (bbl)

also, for encounter rate (area/time):
oil (bbl /hr) = encounter rate (nm²/hr) x slick thickness (mm) x 21,570

Power

1 h.p. = 745 watts = 0.75 kw

Miscellaneous

water density = 62.4 lbs/ft³ or 8.34 lbs/gallon = 1 gm/cc

ice density = 0.8 g/cc or 800 kg/m³

mg/L = parts per million (ppm)

% (expressed as a decimal fraction) x 10⁶ = ppm. (example: 0.7% oil content; 0.007 x 10⁶ = 7,000 ppm)

1 tonne of Corexit 9527 = 263 gallons
1 tonne of Corexit 9500 = 278 gallons

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Appendix B **Manufacturers of Dispersants and Spray Equipment**

Dispersant spray equipment for boats, helicopters, fixed wing aircraft, fire monitors, and single point sources are available from various manufacturers throughout the world. Table B-1 is a representative listing taken and updated from various sources, including the *World Catalog of Oil Spill Response Products* (Ross, 2004). Dispersant application systems differ in design, capability, versatility, size, weight, ease of handling, and control of dosage. Their suitability depends in part on the type of dispersant that is used. Concentrate dispersants are generally most appropriate for modern spray equipment. Table B-2 summarizes the dispersants currently (2007) on the EPA National Contingency Plan Product Schedule. These are the only products currently authorized for use in the US.

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**Table B.1
Manufacturers of Dispersant Spray Systems
for Boats, Helicopters, Fixed Wing Aircraft, and Single Point Systems**

	Boats	Helicopters	Fixed Wing Aircraft	Fire Monitor/ Single Point Systems
ABASCO 3002 Farrell Road Houston, Texas 77073 Tel: 281-443-0927	√	√	√	
Applied Fabric Technology, Inc. 227 Thorn Avenue P.O. Box 575 Orchard Park, New York 14127 Tel: 716-662-0632	√		√	√
Aqua-Guard Spill Response, Inc. #100 – 1055 West 14th Street North Vancouver, British Columbia Canada V7P 3P2 Tel: 604-980-4899	√			√
Ayles Fernie International , Ltd. Unit D5 Chaucer Business Park Kemsing, Seven Oaks, Kent TN15 6YU England Tel: 44/1732762962	√		√	√
Crucial Incorporated 142 Enterprise Drive Gretna, Louisiana 70056 Tel: 540-347-9292	√		√	√
Elastec/American Marine 1309 West Main Carmi, Illinois 62821 Tel: 618-382-2525	√			
KAAF Agro Aviation Les Jasses D'Albaron 13123 Albaror Arles, France Tel: 33/9071188		√		

Table B.1 (continued)

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Manufacturers of Dispersant Spray Systems for Boats, Helicopters, Fixed Wing Aircraft, and Single Point Systems

	Boats	Helicopters	Fixed Wing Aircraft	Fire Monitor/ Single Point Systems
Kepner Plastics Fabricators 3131 Lomita Boulevard Torrance, California 90505 Tel: 310-325-3162	√			
KOLDA Corporation. 123 Northpoint Drive, Suite 189 Houston, Texas 77060 Tel: 281-448-8995	√	√	√	√
Ro-Clean Desmi 21B Hestehaven DK5260, Odense S. Denmark Denmark Tel: 45-65-910-201 UK Tel.: 44 1732 352125 US Tel.: 757-857-3169	√			
Simplex Manufacturing Company 13340 NE Whitaker Way Portland, Oregon 97230 Tel: 503-257-3511		√		
Slickbar Products Corp. 18 Beach Street Seymour, Connecticut 06483 Tel: 203-888-7700	√			√
Vikoma International Ltd. 21/22 Britannia Chambers Town Quay, Southampton, Hampshire SO14 2AQ, UK		√		√

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Table B.2

Dispersants Listed on the EPA NCP Product Schedule for Use in the US (as of 2007)

Dispersant	Manufacturer's Name and Address
BIODISPERS	Petrobiotech LLC P.O. Box 813 Newport, NH 03773 Phone: (203) 966-4573
COREXIT® EC9500A	Nalco Energy Services, L.P. P.O. Box 87 Sugar Land, TX 77487-0087 Phone: (800) 333-3714
COREXIT® EC9527A	Nalco Energy Services, L.P. P.O. Box 87 Sugar Land, TX 77487-0087 Phone: (800) 333-3714
DISPERSIT SPC 1000™	U.S. Polychemical Corp. 584 Chestnut Ridge Road Chestnut Ridge, NY 10977 Phone: (845) 356-5003
FINASOL OSR 52	TOTAL Fluides (TOTAL SA) 51 Esplanade du General de Gaulle 92907 Paris-La-Devence France Phone: +33 (0) 1-4135-6123
JD-109	GlobeMark Resources Ltd. 957 Nasa Parkway, #221 Houston, TX 77058 Mobile: (254)231-2251
JD-2000™	GlobeMark Resources Ltd. 957 Nasa Parkway, #221 Houston, TX 77058 Mobile: (254)231-2251
Mare Clean 200	Taiho Industries Co. Ltd. 21-44, 2-chome, Takanawa Minatoku, Tokyo, Japan Phone: (81) 33-445-8111

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Table B.2 (continued)
Dispersants Listed on the EPA NCP Product Schedule for Use in the US (as of 2007)

Dispersant	Manufacturer's Name and Address
NEOS AB3000	NEOS Company Limited Daisan Kendai Building 1-2, 3-chome Isobedori Chuo-ku, Kobe, Japan 651-0084 Phone: (81) 78-331-9384
NOKOMIS 3-F4	Mar-Len Supply, Inc 23159 Kidder Street Hayward, CA 94545 Phone: (510) 782-3555
SAF-RON GOLD	Saf-Ron International, Inc. P.O. Box 690172 Houston, TX 77069-0172 Phone/Fax: (877) 853-2947
SEA BRAT #4	Alabaster Corp. 6921 Olson Ln. Pasadena, TX 77505 Phone: (281) 487-5482
ZI-400	Z.I. Chemicals P.O. Box 1112 Studio City, CA 91614-1112 Phone: (818) 770-6225

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Table B.3
Dispersants Approved for Use in the United Kingdom (as of 2007)

Dispersant	Manufacturer's Name and Address
AGMA DR 379	Agma plc Gemini Works Haltwhistle Northumberland NE49 9HA Phone: (44) 1434 320598
AGMA OSD 569	Agma plc Gemini Works Haltwhistle Northumberland NE49 9HA Phone: (44) 1434 320598
CAFLON OSD	Univar Ltd Pine Street South Bank Road Middleborough, Cleveland TS3 8BD Phone: (44) 1642 227388
COMPOUND W-2096	Baker Petrolite LTD Kirkby Bank Road Knowsley Industrial Park (North) Liverpool L33 7SY Phone: (44) 151 546 2855
DASIC SLICKGONE EW	Dasic International Ltd Winchester Hill Romsey Hants SO51 7YD Phone: (44) 1794 512419
DASIC SLICKGONE NS	Dasic International Ltd Winchester Hill Romsey Hants SO51 7YD Phone: (44) 1794 512419

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Dispersant	Manufacturer's Name and Address
ENERSPERSE 1040	Darcy Industries Ltd Riversdale Mill Hacken Lane Darcy Lever Bolton BL3 1SJ Phone: (44) 1204 552 612
FINASOL OSR 51	Total Fluides 51, Esplanade du General de Gaulle 92907 Paris La Defence Cedex, France Phone: (33) 1 41 35 22 74
FINASOL OSR 52	Total Fluides 51, Esplanade du General de Gaulle 92907 Paris La Defence Cedex, France Phone: (33) 1 41 35 22 74
GARD SLICKSOL	Larragard Ltd Chapel Lane Heckmondwike West Yorkshire WF16 9JP Phone: (44) 1924 403550
MAXI-CLEAN 2	Nalfleet Marine Chemicals PO Box 11 Northwich, Cheshire CW8 4DX Phone: (44) 1606 721509
NU CRU	Ara Chem Inc. Box 5031 San Diego, CA 92165 USA Phone: (619) 286 4131
OD 4000	Innospec Ltd 17 Route de Rouen 27950 Saint Marcel France Phone: (33) 2 32 64 35 35
Dispersant	Manufacturer's Name and Address

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OSR 4000	Innospec Ltd 17 Route de Rouen 27950 Saint Marcel France Phone: (33) 2 32 64 35 35
RADIAGREEN OSD	Oleon N.V. Industriezone Ter Straten Vaartstraat 130 B-2520 Oelegem, Belgium Phone (32) 3 470 6272
SEACARE ECOSPERSE	Unitor Chemicals Kjemi-Service AS PO Box 49 N-3163 Borgheim Norway Phone: (47) 33 35 1599
SEACARE OSD	Unitor Chemicals Kjemi-Service AS PO Box 49 N-3163 Borgheim Norway Phone: (47) 33 35 1599
SUPER-DISPERSANT 25	Oil Slick Dispersants Ltd Beck Cottage Main Street, Elvington York YO41 4AG Phone: (44) 1904 607910
VECLEAN OIL DISPERSANT	Westchem B.V. Mozartlaan 3 3144 NA Maassluis The Netherlands Phone: (31) 1059 30240

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Table B.4
Dispersants Approved for Use in France (as of 2007)

(Courtesy of Cedre. A complete listing of dispersants approved in the European Union Member States can be found in European Maritime Safety Agency, 2005)

Dispersant	Manufacturer's Name and Address
BIOREICO R93	Reico 13, rue de la Libération 28210 Villemeux sur Eure F France Phone: (33) 2 37 65 80 69
COREXIT 9500	Nalco Energy Services, L.P. P.O. Box 87 Sugar Land, TX 77487-0087 Phone: (1) 800-333-3714
DASIC SLICKGONE NS	Dasic International Ltd Winchester Hill Romsey Hants SO51 7YD Phone: (44) 1794 512419
DISPEREP 12	REP International 40, avenue Jean Jaurès ZI Pétrolière 78440 Issou Gargenville France Phone: (33) 1 30 98 80 00
DISPER M	Zep Industries Z.I. du Poirier Rue Nouvelle 28210 Nogent le Roi France Phone: (33) 2 37 65 50 50
DISPOLENE 36S	Ste Seppic/Air Liquide Tour Kupka C 7, boulevard Franck Kupka 92039 Paris La Défense Cédex Phone: (33) 1 55 91 57 76

ExxonMobil Oil Spill Dispersant Guidelines

Table B.4 (continued)
Dispersants Approved for Use in France (as of 2007)

(Courtesy of Cedre)

Dispersant	Manufacturer's Name and Address
EMULGAL C-100	Amgal Chemical Products 1989 Ltd 2 Haharash Street Ness-Ziona 74031 Israel Phone: (972) 89308320
FINASOL OSR 51 FINASOL OSR 52 FINASOL OSR 61 FINASOL OSR 62	Total Fluides 51, Esplanade du Général de Gaulle La Défense 10 F-92907 Paris La Défense Phone: (33) 1 41 35 59 83 (33) 1 41 35 31 01
OD 4000 (PE 998)	Innospec Ltd 17, route de Rouen 27950 Saint Marcel F Phone: (33) 2 32 64 35 25
INIPOL IP 80 INIPOL IP 90 INIPOL IPC	CECA 4-8, COURS Michelet – La Défense 10 F-92091 Paris La Défense Cedex Phone: (33) 1 49 00 37 82
NEUTRALEX C	Société Industrielle de Diffusion 2, rue Antoine Etex 94020 Créteil F Phone: (33) 1 45 17 43 00
NU CRU	Gold Crew Products and Services Box 5031 San Diego, Calif. 92165-5031 USA Phone: (1) 619 286 4131
OCEANIA 1000	Henkel Technologies Buroparc – Bâtiment B 3, allée Emile Reynaud 77200 Torcy F Phone: (33) 1 60 17 02 02 (33) 1 60 17 66 40

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Table B.4 (continued)
Dispersants Approved for Use in France (as of 2007)

(Courtesy of Cedre)

Dispersant	Manufacturer's Name and Address
RADIAGREEN OSD	Oleon N.V. Industriezone Ter Straten Vaartstraat 130 B-2520 Oelegem, Belgium Phone (32) 3 470 6272
O.S.D. - 2B	C.A.M.I. 1ère avenue n °44 Z.I. 13127 Vitrolles F Phone: (33) 4 42 89 18 50

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Table B.5
Dispersants Approved for Use in Australia (as of 2008)

(Courtesy of AMSA)

Dispersant	Manufacturer's Name and Address
ARDROX 6120	SureChem Industries Pty Ltd 23 Amax Ave Girraween 2146 NSW, Australia Phone: (61) 2 9896 0700
BP-AB	BP Australia Pty Ltd A.B.N. 53 004 085 616 Melbourne Central 360 Elizabeth Street Melbourne, Victoria 3000 Phone: (61) 3 9268 4111
COREXIT 9500 COREXIT 9527 COREXIT 9550	Nalco Energy Services, L.P. P.O. Box 87 Sugar Land, TX 77487-0087 USA Phone: (1) 800-333-3714
SHELL VDC	Shell Company of Australia Ltd A.B.N. 46 004 610 459 Level 2, 8 Red Fern Road Hawthorne East Victoria 3123 Phone (61) 3 9666 5444
SLICKGONE NS	Dasic International Ltd Winchester Hill Romsey, Hants UK SO51 7YD Phone: (44) 1794 512419
TERGO R-40	Tergo Industries Ltd PO Box 15783 New Lynn Auckland, New Zealand Phone: Mob. 027 435 9411 or 021 950 958

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Appendix C

Discussion Paper on Dispersant Toxicity

by ExxonMobil's Jim Clark and Anita George-Ares

In a review of worldwide dispersant policy issues, Etkin (1999) reported that more than 73% of 150 nations surveyed "specifically allow dispersant usage." Many of these countries utilize some sort of laboratory testing as part of a review/registration process required before approval for use can be obtained. Development of a national system of dispersant approval typically involves a wide range of environmental, safety, and application considerations, often leading to some form of general restrictions or limitations on where and when dispersants might be used. There may be additional, specific restrictions on use in areas of special environmental concern or areas with limited depth, mixing or flushing characteristics. Restrictions may also address special notification procedures for obtaining permission to use dispersants for an incident.

Toxicity Testing Issues

Toxicity is not a fixed attribute of dispersants. As defined by Rand, et al, (1995), toxicity is a relative quality of a substance, reflecting a potential for harmful effects based on the nature and duration of an organism's exposure, and the concentrations encountered during the period of exposure. A number of physiological and biochemical mechanisms exist by which substances may exert toxic effects on organisms. These "modes of action" have a significant influence on how toxic effects are observed. Toxic effects can range from short-term to longer-term, and from direct lethality to development of more subtle changes in biological or physiological functions, or damage to an organism's tissues, cells or cell structures. Acute lethal response (observed deaths during 1-4 days of exposure) is the most frequent measure of toxic effect in laboratory studies, due to its ease of use for a wide variety of species, lower cost, high repeatability, and availability of widely accepted standardized testing methods.

The expression of toxicity is specific for the population of test organisms studied, their age, health, prior exposure history, and many other factors. Results may differ for toxicity tests conducted under different environmental conditions, or with different groups of organisms. Thus the usefulness and relevancy of laboratory toxicity data for environmental decision-making must be considered in the context of numerous factors. It is important to understand: 1) the life history and biological cycles of the species tested, 2) the species' ability to survive and grow under the conditions of laboratory control, and 3) the extent to which external environmental factors such as temperature, salinity, pH, dissolved oxygen, light intensity, etc, can alter the species' ability to tolerate exposure to chemical substances. Toxicity data from one species may provide insight into the potential harm a substance may pose for another species that possesses a close evolutionary link (same genus, same family). However, closely linked species could still have significantly different exposure patterns, metabolic capabilities or sufficiently different life history strategies that would make their toxicological sensitivities very different.

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Useful Generalities

Despite all these concerns and variability, there are some broad generalities that can be useful when one examines large datasets of toxicity data for groups of chemicals. Even more generalities are evident if considerations are restricted to toxic effects of oil and dispersants, because the possible modes of toxic action are more defined among specific types of substances.

Petroleum -- When considering toxic effects of petroleum, among the more important factors that can be observed is that toxicity generally increases with increased duration of exposure, although not necessarily in a directly scaled or proportional rate. Younger organisms tend to be more sensitive than adults of the same species. Species with less evolved or less sophisticated metabolic systems (mollusks, echinoderms) tend to be more sensitive to oil than more highly evolved species (fishes, crustaceans). Also, for these more highly evolved species, sub-lethal effects of short-term exposure usually are quickly reversed (animals recover faster) after the exposure to petroleum ends.

Dispersants (Surfactants) -- The main ingredients in dispersant formulations are surface active agents, called surfactants. In short-term exposures where lethality is the effect endpoint, surfactants tend to show an all-or-none response; that is, once a toxic threshold concentration has been reached, an effect is observed. Additional exposure times at lower concentrations may not lead to significant increases in mortality. Larvae and juvenile life stages tend to be much more sensitive to surfactants than adults of the same species. In short-term exposures, surfactants act as irritating agents on tissues and cell membranes (gills, gut linings, skin surfaces); however, toxicity observed from longer-term exposures can be derived from a number of mechanisms.

Toxicity Tests and Dispersant Approval Decisions

Table C-1 lists a number of countries that use toxicity test data as part of the dispersant approval decision. Different countries use differing combinations of tests on fishes, invertebrates or algae. It is important to note that most common dispersants being considered for use have been tested in at least a few countries and are registered for use there. In countries where dispersants are approved, the approval for use is not based on the fact that an LC₅₀ can be generated; rather, the toxicity information is used to identify the nature of environmental concerns associated with the dispersant. That effort then formulates specific use recommendations or restrictions on dispersant use.

It is also important to remember that the toxicity of a crude oil or refined fuel, either chemically dispersed or naturally dispersed, generally is greater than that of the dispersants. Therefore, the decision to use dispersants should focus on the net environmental benefit of moving the oil into the water column where it can be quickly diluted and the marine life can recover quickly, compared to the potentially greater impacts of the oil becoming stranded in intertidal or shoreline habitats.

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Table C-1. Toxicity Testing Requirements for Dispersant Approval in Various Countries.

Country	Fish Test	Crustacean Test	Algae Test
United Kingdom		✓	
France	✓	✓	
Norway	✓	✓	✓
United States	✓	✓	
Australia	✓	✓	
Brazil	✓	✓	
Japan	✓		✓
Argentina	✓	✓	

Applying Toxicity Data for Dispersant Registration/Approval Decisions

Various parameters should be considered when reviewing toxicity data on dispersants in the context of registration or approval decisions. When used for comparative purposes only, toxicity data can assist in selection of the lower toxicity products, if all other factors are equal. Unfortunately, it is rarely that simple; all other factors are not equal. The effectiveness of dispersants on a range of oil types and on fresh and weathered oil should play a significant role in use decisions. Dispersant products vary greatly in their capabilities to effectively disperse various types of oils. It is prudent to stockpile the dispersant that has the greatest chance of being effective on a range of crude oils and refined oils (fuels, lubricants) that might be spilled. In addition, the cost and availability of dispersants, their shelf life, application and handling consideration should also be factored into a decision. In fact, when the dispersant toxicity is less than that of dispersed oil (which is the case for modern dispersant formulations), dispersant toxicity is rarely a deciding factor in use decisions. Such is the case in the United States and Brazil. In these countries, toxicity data are collected and considered, but there is no regulatory acceptance criteria based on toxicity; rather, the focus is on approving products that demonstrate a high degree of effectiveness.

Published Toxicity Data for Corexit Dispersants

Attached are a series of tables that review published toxicity values for the Corexit dispersants. The data in these tables come mostly from laboratory studies conducted by research organizations interested in the toxicity of dispersants to marine organisms, and organizations that publish test results in technical journals. What are missing in these data tables are results of toxicity tests used to register the dispersants in various countries. Those data are not available because only a

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few of the countries that require toxicity testing for dispersant registration also make those data available to the public.

The data tables are intended to document the range of toxicity values that have been reported for the Corexit dispersants, demonstrating the high degree of variability in reported toxicity values. Most of the variance comes from the variety of test methods, species and life stages used for testing. The significance of these sources of variance is discussed by George-Ares and Clark (2000). Because Corexit products are the most widely approved, stocked, and used dispersants in the world, they have been studied much more extensively than other products. Therefore, they have significantly more published data available compared to the other dispersants.

References:

- Rand, G. M., P.G. Wells and L.S. McCary. 1995. "Introduction to Aquatic Toxicology." In **Fundamentals of Aquatic Toxicology Second Edition** (Edited by G. M. Rand), p. 1-67 Taylor and Francis, Washington, DC.
- Etkin, D.S. 1999. **Oil Spill Dispersants: From Technology to Policy**. Cutter Information Corp., Arlington, MA, USA.
- George-Ares, A. and J. R. Clark. 2000. "Aquatic Toxicity of Two Corexit Dispersants." **Chemosphere** 40:897-906.

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Appendix C Data Tables

Overview of Published Data for Corexit Dispersants

(Data from standard 24-96 hr. LC50 or EC 50 in mg/L*)

Summary

Dispersants	Fish Data (mg/L)	Invertebrate Data (mg/L)	Algae Data (mg/L)
Corexit 9527	14.3-150 (12 species)	1.6-81 (7 species)	30-80 (2 species)
Corexit 9500	20- > 400 (9 species)	14-83 (10 species)	0.7-20 (2 species)

The following notes apply to Tables C-2 and C-3:

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F = field collected

SD = spiked, declining exposure (107 min half-life)

EC₅₀ = concentrations causing effect in 50% of organisms

LC₅₀ = concentration causing mortality in 50% of organisms

IC₅₀ = concentration causing inhibition in 50% of organisms

NOEC = no effect concentration

***measured values**

Table C-2. Aquatic Toxicity of Corexit ® 9527

Common Name ¹	Species	Exposure ² (hrs)	Endpoint ³	Effect Concentration (ppm)	Reference
Crustaceans					
Brine Shrimp	<i>Artemia</i> sp.	48	LC ₅₀	52 to 104	9
Brine Shrimp	<i>Artemia salina</i>	48	LC ₅₀	53 to 84	10
Isopod, F	<i>Gnoringospaeroma oregonensis</i>	96	LC ₅₀	> 1,000	11
Amphipod, F	<i>Anonyx laticoxae</i>	96	LC ₅₀	> 140	12
Amphipod, F	<i>Anonyx nugax</i>	96	LC ₅₀	97 to 111	12
Amphipod, F	<i>Boeckosimus</i> sp.	96	LC ₅₀	> 175	12
Amphipod, F	<i>Boeckosimus edwardsi</i>	96	LC ₅₀	> 80	12
Amphipod, F	<i>Onisimus litoralis</i>	96	LC ₅₀	80 to 160	12
Amphipod, (juvenile), F	<i>Gammarus oceanicus</i>	96	LC ₅₀	> 80	12
Amphipod, F	<i>Allorchestes compressa</i>	96	LC ₅₀	3.0	13
Copepod, F	<i>Pseudocalanus minutus</i>	48	LC ₅₀	8 to 12	9
Copepod, F	<i>Pseudocalanus minutus</i>	96	LC ₅₀	5 to 25	9

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Table C-2. Aquatic Toxicity of Corexit ® 9527

Common Name ¹	Species	Exposure ² (hrs)	Endpoint ³	Effect Concentration (ppm)	Reference
Grass Shrimp, F	<i>Palaemonetes pugio</i>	96	LC50	640 (27 oC)	2
Grass Shrimp, F	<i>Palaemonetes pugio</i>	96	LC50	840 (17 oC)	2
Giant Freshwater Prawn (Embryo-Larval)	<i>Macrobrachium rosenbergii</i>	288	EC50 Hatching	80.4	14
Prawn	<i>Penaeus monodon</i>	96	LC50	35 to 45	15
Whiteleg Shrimp	<i>Penaeus vannamei</i>	96	LC50	35 to 45	15
White Shrimp (Postlarvae), F	<i>Penaeus setiferus</i>	96	LC50	11.9	15
Gulf Mysid	<i>Mysidopsis bahia</i>	96	LC50	29.2*, 19 to 34	10, 16,17,18
Gulf Mysid	<i>Mysidopsis bahia</i>	48	LC50	24.1	19
Gulf Mysid	<i>Mysidopsis bahia</i>	SD	LC50	> 1,014*	1
Kelp Forest Mysid, F	<i>Holmesimysis costata</i>	96	LC50	2.4* to 10.1*	18, 20, 21
Kelp Forest Mysid, F	<i>Holmesimysis costata</i>	SD	LC50	195*	22
Kelp Forest Mysid, F	<i>Holmesimysis costata</i>	96	LC50	4.3* to 7.3*	6, 7
Kelp Forest Mysid, F	<i>Holmesimysis costata</i>	SD	LC50	120* to 163*	7
Kelp Forest Mysid	<i>Holmesimysis costata</i>	96	LC50	15.3*	23
Blue Crab (Larvae), F	<i>Callinectes sapidus</i>	96	LC50	77.9 to 81.2	15
Ghost shrimp, F	<i>Palaemon serenus</i>	96	LC50	49.4	53
Mollusks					
Scallop, F	<i>Argopecten irradians</i>	6	LC50	200 (20 oC)	24

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Table C-2. Aquatic Toxicity of Corexit ® 9527

Common Name ¹	Species	Exposure ² (hrs)	Endpoint ³	Effect Concentration (ppm)	Reference
Scallop, F	Argopecten irradians	6	LC50	1,800 (10 oC)	24
Scallop, F	Argopecten irradians	6	LC50	2,500 (2 oC)	24
Red Abalone (Embryos)	Haliotis rufescens	48	EC50	1.6* to 2.2*	6, 7
Red Abalone (Embryos)	Haliotis rufescens	SD	EC50	13.6* to 18.1*	7
Clam, F	Protothaca staminea	96	LC50	ca.100	25
Pacific oyster (Embryos)	Crassostrea gigas	48	LC50	3.1*	22
Pacific oyster (Embryos)	Crassostrea gigas	SD	LC50	13.9*	22
Marine Sand Snail, F	Polinices conicus	24	EC50	33.8	13
Fish					
Medaka	Oryzias latipes	24	LC50	130 to 150 seawater 400 freshwater	26
Rainbow Trout	Oncorhynchus mykiss	96	LC50	96 to 293	27
Spot (Embryos)	Leiostomus xanthurus	48	LC50	61.2 to 62.3	28
Spot (Embryo-Larval), F	Leiostomus xanthurus	48	LC50	27.4	15
Top Smelt (Larvae)	Atherinops affinis	96	LC50	25.5* to 40.6*	6, 7
Top Smelt (Larvae)	Atherinops affinis	SD	LC50	59.2* to 104*	7
Fourhorn Sculpin, F	Myoxocephalus quadricornis	96	LC50	< 40	12

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Table C-2. Aquatic Toxicity of Corexit ® 9527

Common Name ¹	Species	Exposure ² (hrs)	Endpoint ³	Effect Concentration (ppm)	Reference
Mummichog	Fundulus heteroclitus	96	LC50	99 to 124	10
Inland Silverside (Larvae)	Menidia beryllina	96	LC50	52.3*, 14.6 to 57	10, 15, 18, 19, 29
Inland Silverside (Larvae)	Menidia beryllina	SD	LC50	58.3*	22
Inland Silverside (Embryos)	Menidia beryllina	96	LC50	> 100	15
Red Drum (Embryo-Larva),F	Sciaenops ocellatus	48	LC50	52.6	15
Sheepshead Minnow	Cyprinodon variegatus	96	LC50	74 to 152	10
Atlantic Menhaden (Embryo-Larva),F	Brevoortia tyrannus	48	LC50	42.4	15
Australian Bass (larvae)	Macquaria novemaculeata	96	LC50	14.3	53
Mexican Molly	Poecilia sphenops	96	LC50	39.9	55
Hydrozoan					
Green Hydra	Hydra viridissima	96	LC50	230*	52
Seagrass					
Turtlegrass, F	Thalassia testudinum	96	LC50	200	30
Macroalgae					
Giant Kelp (Zoospores), F	Macrocystis pyrifera	48	NOEC	1.3* to 2.1*	6, 7
Giant Kelp (Zoospores), F	Macrocystis pyrifera	SD	NOEC	12.2* to 16.4*	7
Giant Kelp (Zoospores), F	Macrocystis pyrifera	SD	IC50	86.6* to 102*	7

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Table C-2. Aquatic Toxicity of Corexit ® 9527

Common Name ¹	Species	Exposure ² (hrs)	Endpoint ³	Effect Concentration (ppm)	Reference
Brown alga	Phyllospora comosa	48	EC50	30	31
Bacteria					
Microtox™	Vibrio fisheri	0.25	EC50	4.9 to 12.8	16, 32

Table C-3. Aquatic Toxicity of Corexit ® 9500

Common Name ¹	Species	Exposure ² (hrs)	Endpoint ³	Effect Concentration (ppm)	Reference
Crustaceans					
Amphipod, F	Allorchestes compressa	96	LC ₅₀	3.5	13
Brine Shrimp	Artemia salina	48	LC ₅₀	21	33
White Shrimp, F	Palaemonetes varians	6	LC ₅₀	8,103	34
Gulf Mysid	Mysidopsis bahia	48	LC ₅₀	32.2	19
Gulf Mysid	Mysidopsis bahia	96	LC ₅₀	35.9*	22
Gulf Mysid	Mysidopsis bahia	96	LC ₅₀	29.1	56
Gulf Mysid	Mysidopsis bahia	SD	LC ₅₀	> 789* to 1,038*	8
Gulf Mysid	Mysidopsis bahia	SD	LC ₅₀	330.7	56
Copepod (adult)	Eurytemora affinis	96	LC ₅₀	5.2*	35
Kelp Forest Mysid, F	Holmesimysis costata	SD	LC ₅₀	158* to 245*	36
Kelp Forest Mysid, F	Holmesimysis costata	SD	NOEC	41.4* to 142*	36
Prawn (larval) , F	Penaeus monodon	96	LC ₅₀	48	37

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Table C-3. Aquatic Toxicity of Corexit ® 9500

Common Name ¹	Species	Exposure ² (hrs)	Endpoint ³	Effect Concentration (ppm)	Reference
Ghost Shrimp, F	<i>Palaemon serenus</i>	96	LC ₅₀	83.1	53
Tanner Crab (Larvae)	<i>Chionoecetes bairdi</i>	SD	EC ₅₀	1,267	56
Tanner Crab (Larvae)	<i>Chionoecetes bairdi</i>	96	EC ₅₀	23.8	56
Molluscs					
Marine Sand Snail, F	<i>Polinices conicus</i>	24	EC ₅₀	42.3	13
Red Abalone (Embryos)	<i>Haliotis rufescens</i>	48	NOEC	0.7*	38
Red Abalone (Embryos)	<i>Haliotis rufescens</i>	SD	NOEC	5.7* to 9.7*	36
Red Abalone (Embryos)	<i>Haliotis rufescens</i>	SD	LC ₅₀	12.8* to 19.7*	36
Fish					
Barramundi (juvenile)	<i>Lates calcarifer</i>	96	LC ₅₀	143	37
Turbot (yolk-sac larvae)	<i>Scophthalmus maximus</i>	48	LC ₅₀	74.7*	22
Turbot (yolk-sac larvae)	<i>Scophthalmus maximus</i>	SD	LC ₅₀	> 1,055*	22
Rainbow Trout	<i>Oncorhynchus mykiss</i>	96	LC ₅₀	354	39
Mummichog	<i>Fundulus heteroclitus</i>	96	LC ₅₀	140	33
Mozambique Tilapia	<i>Sarotherodon mozambicus</i>	96	LC ₅₀	150	26
Zebra Danio	<i>Brachydanio rerio</i>	24	LC ₅₀	> 400	40

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Table C-3. Aquatic Toxicity of Corexit ® 9500

Common Name¹	Species	Exposure² (hrs)	Endpoint³	Effect Concentration (ppm)	Reference
Australian Bass (larvae)	Macquaria novemaculeata	96	LC ₅₀	19.8	53
Inland Silverside (larvae)	Menidia beryllina	96	LC ₅₀	25.2	19
Inland Silverside	Menidia beryllina	96	LC ₅₀	54.7	56
Inland Silverside	Menidia beryllina	SD	LC ₅₀	115.2	56
Hardy Heads (Juvenile), F	Atherinosoma microstoma	96	LC ₅₀	50	37
Hydrozoan					
Green Hydra	Hydra viridissima	96	LC ₅₀	160*	52
Algae					
Diatom	Skeletonema costatum	72	EC ₅₀	20	41
Brown Alga (Zygotes), F	Phyllospora comosa	48	EC ₅₀	0.7	31

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Dispersant Toxicity References

1. C. B. Pace, J. R. Clark and G. E. Bragin, Comparing crude oil toxicity under standard and environmentally realistic exposures, *Proceedings 1995 International Oil Spill Conference*, p. 1003-1004. American Petroleum Institute, Washington, D. C. (1995).
2. National Research Council, *Using Oil Spill Dispersants on the Sea*, Chap. 3, National Academy Press, Washington, D. C. (1989).
3. ASTM. *Annual Book of Standards*, Vol. 11.04, Section F. West Conshohoken, Pennsylvania (2007).
4. A. Lewis and D. Aurand, *Putting Dispersants to Work: Overcoming Obstacles*, API Publ. 4652A, American Petroleum Institute, Washington, D.C. (1997).
5. M. M. Singer, D. L. Smalheer and R. S. Tjeerdema, A simple continuous-flow toxicity test system for microscopic life stages of aquatic organisms, *Water Research* **24**, 899-903 (1990).
6. M. M. Singer, D. L. Smalheer, R. S. Tjeerdema and M. Martin, Toxicity of an oil dispersant to the early life stages of four California marine species, *Environ. Tox. Chem.* **9**, 1389-1397 (1990).
7. M. M. Singer, D. L. Smalheer, R. S. Tjeerdema and M. Martin, Effects of spiked exposure to an oil dispersant on the early life stages of four marine species, *Environ. Tox. Chem.* **10**, 1367-1374 (1991).
8. G. M. Coelho and D. V. Aurand, editors. *Proceedings. 6th Meeting of the Chemical Response to Oil Spills: Ecological Effects Research Forum*. Ecosystem Management & Associates, Purcellville, Virginia (1997).
9. P. G. Wells, S. Abernethy and D. Mackay, Study of oil water partitioning of a chemical dispersant using an acute bioassay with marine crustaceans, *Chemosphere* **11**, 1071-1086 (1982).
10. J. Briceno, W. J. McKee, J. R. Clark and D. D. Whiting, Relative sensitivity of Gulf of Mexico species and national test species in acute toxicity tests with dispersants. Poster presentation. *13th Annual Meeting, Society of Environmental Toxicology and Chemistry*, Cincinnati, Ohio (1992).
11. W. S. Duval, L. A. Harwood and R. P. Fink, The sublethal effects of dispersed oil on an estuarine isopod. Technology Development Report, EPS-4-EC-82-1, Environment Canada, Ottawa (1982).

ExxonMobil Oil Spill Dispersant Guidelines

12. M. G. Foy, Acute lethal toxicity of Prudhoe Bay Crude oil and Corexit 9527 to Arctic marine fish and invertebrates, Technology Development Report, EPS 4-EC-82-3, Environment Canada, Ottawa (1982).
13. I. Gulec, B. Leonard and D. A. Holdway, Oil and dispersed oil toxicity to amphipods and snails, *Spill Sci. Tech. Bull.* **4**, 1-6 (1994).
14. A. T. Law, Toxicity study of the oil dispersant Corexit 9527 on *Macrobrachium rosenbergii* (de Man) egg hatchability by using a flow-through bioassay technique, *Environ. Pollut.* **88**, 341-343 (1995).
15. K. W. Fucik, K. A. Carr and B. J. Balcom. Toxicity of oil and dispersed oil to the eggs and larvae of seven marine fish and invertebrates from the Gulf of Mexico, *The Use of Chemicals in Oil Spill Response*, (Edited by P. Lane), p. 135-171. American Society for Testing and Materials. Philadelphia, Pennsylvania (1995).
16. A. George-Ares, J. R. Clark, G. R. Biddinger and M. L. Hinman. A comparison of test methods and early toxicity characterization for five dispersants, *Ecotox. Environ. Safety* **42**, 138-142 (1999).
17. ExxonMobil Biomedical Sciences, Inc., Mysid acute toxicity test. Flow-through continuous exposure with *Mysidopsis bahia*. Test material: Corexit 9527, East Millstone, New Jersey (1993a).
18. C. B. Pace and J. R. Clark, Evaluation of a toxicity test method used for dispersant screening in California, MSRC Technical Report Series 93-028, Marine Spill Response Corp., Washington, D. C. (1993).
19. Inchcape Testing Services, Laboratory test data for Corexit 9500 and Corexit 9527 Houston, Texas (1995).
20. Exxon Biomedical Sciences, Inc. Mysid acute toxicity test, Continuous exposure with *Holmesimysis costata*, Test material, Corexit[®] 9527, Clinton, New Jersey (1993b).
21. Exxon Biomedical Sciences, Inc. Mysid acute toxicity test, Flowthrough continuous exposure with *Holmesimysis costata*, Test material, Corexit 9527, East Millstone, New Jersey (1993c).
22. G. E. Bragin and J. R. Clark, Unpublished data for Corexit 9500 and Corexit 9527. Manuscript in preparation, Exxon Biomedical Sciences, Inc., East Millstone, New Jersey.

ExxonMobil Oil Spill Dispersant Guidelines

23. G. M. Coelho and D. V. Aurand, editors. *Proceedings 5th Meeting of the Chemical Response to Oil Spills: Ecological Effects Research Forum*. Ecosystem Management & Associates, Purcellville, Virginia (1996).
24. C. J. Ordsie and G. C. Garofalo, Lethal and sublethal effects of short term acute doses of Kuwait crude oil and a dispersant Corexit 9527 on bay scallops *Argopecten irradians* and two predators at different temperatures, *Mar. Environ. Res.* **5**, 195-210 (1981).
25. E. B. Hartwick, R. S. S. Wu and D. B. Parker, Effects of a crude oil and an oil dispersant Corexit 9527 on populations of the littleneck clam *Protothaca staminea*, *Mar. Environ. Res.* **6**, 291-306 (1982).
26. R. R. Lessard. Personal communication, Exxon Research and Engineering Company, Florham Park, New Jersey (Jan. 17 and May 4, 1995).
27. P. Wells and K. G. Doe, Results of the E.P.S. oil dispersant testing program: concentrates, effectiveness testing, and toxicity to marine organisms, *Spill Technol. Newsletter* **1**, 9-16 (1976).
28. G. J. Slade, Effect of Ixtoc I crude oil and Corexit[®] 9527 on spot (*Leiostomus xanthurus*) egg mortality, *Bull. Environ. Contam. Toxicol.* **29**, 525-530 (1982).
29. ExxonMobil Biomedical Sciences, Inc., Fish acute toxicity test flowthrough continuous exposure with *Menidia beryllina*, Test material, Corexit 9527, Clinton, New Jersey (1993d).
30. B. J. Baca and C. D. Getter. The toxicity of oil and chemically dispersed oil to the seagrass *Thalassia testudinum*. In *Oil Spill Chemical Dispersants: Research, Experience, and Recommendations*, (Edited by T. E. Allen), p. 314-323, American Society for Testing and Materials, Philadelphia, Pennsylvania (1984).
31. T. R. Burrige and M. Shir, The comparative effects of oil, dispersants, and oil/dispersant conjugates on germination of marine macroalga *Phyllospora comosa* (Fucales:Phaeophyta), *Mar. Pollut. Bull.* **31**, 446-452 (1995).
32. ExxonMobil Biomedical Sciences, Inc., Microtox[®] toxicity tests. Test material: Corexit 9527, Clinton, New Jersey (1992).
33. United States Testing Company, Inc., Report No. 066234 (1994).
34. C. Beaupoil and D. Nedelec, Etude de la toxicite du produit de lavage Corexit[®] 9500 vis-a-vis de la crevette blanche *Palaemonetes varians*, Laboratoire de Biologie Marine, Concarneau, France (1994).

ExxonMobil Oil Spill Dispersant Guidelines

35. D. A. Wright and G. M. Coehlo, Dispersed oil and dispersant fate and effects research: MD program results for 1995, MSRC Technical Report Series 95-013. Draft report, Marine Spill Response Corp., Washington D.C. (1996).
36. M. M. Singer, S. George, S. Jacobson, I. Lee, L. L. Weetman, R. S. Tjeerdema and M. L. Sowby, Comparison of acute aquatic effects of the oil dispersant Corexit 9500 with those of other Corexit series dispersants, *Ecotox. Environ. Safety* **35**, 183-189 (1996).
37. Marine and Freshwater Resources Institute, Toxicity and effectiveness of the oil spill dispersant Corexit 9500, Laboratory report, Queenscliff, Australia (1998).
38. Aquatic Testing Laboratories, Abalone larval development short term toxicity test for oil spill cleanup agents, Laboratory report, Ventura, California (1994).
39. Environment Canada, Laboratory aquatic toxicity data for Corexit 9500, File 4808-13-1, Ottawa, Ontario (April 27, 1994).
40. M. A. Walsh, Personal communication, Nalco/Exxon Energy Chemicals, L. P. Sugar Land, Texas (June 7, 1995).
41. Norwegian Institute for Water Research, Marine algal growth inhibition test, Laboratory Report, Oslo, Norway (1994).
42. G. M. Rand and S. R. Petrocelli, Introduction. In *Fundamentals of Aquatic Toxicology* (Edited by G. M. Rand and S. R. Petrocelli), p. 1-28 Hemisphere Publishing Corp., New York (1985).
43. J. B. Sprague. Factors that modify toxicity. In *Fundamentals of Aquatic Toxicology* (Edited by G. M. Rand and S. R. Petrocelli), p. 124-163. Hemisphere Publishing Corp., New York (1985).
44. W. S. Fisher and S. S. Foss, A simple test for toxicity of number 2 fuel oil and oil dispersants to embryos of grass shrimp, *Palaemonetes pugio*, *Mar. Pollut. Bull.* **26**, 385-391 (1993).
45. J. R. Sharp, K. W. Fucik and J. M. Neff, Physiological basis of differential sensitivity of fish embryonic stages to oil pollution. In *Marine Pollution: Functional Responses* (Edited by W. B. Vernberg, A. Calabrese, F. P. Thurberg, and F. J. Vernberg), p. 85-108, Academic Press, New York (1979).
46. O. Lindén, Effects of oil spill dispersants on the early development of Baltic herring, *Ann. Zool. Fennici* **11**, 141-148 (1974).

ExxonMobil Oil Spill Dispersant Guidelines

47. L. Weetman, M. Singer, S. George, S. Jacobson, R. Tjeerdema and M. L. Sowby, Evaluation of dispersant toxicity using a standard modeled-exposure approach, *Proceedings 1995 International Oil Spill Conference*, American Petroleum Institute, pp. 830-832. Washington, D. C. (1995).
48. C. Bocard, G. Castaing and C. Gatellier, Chemical oil dispersion in trials at sea and in laboratory tests: the key role of dilution processes, *Oil Spill Chemical Dispersants, Research, Experience, and Recommendation*, p. 125-142. American Society for Testing and Materials. (Edited by T. E. Allen) Philadelphia, Pennsylvania (1984).
49. G. M. Scelfo and R. S. Tjeerdema, A simple method for determination of Corexit 9527 in natural waters, *Mar. Environ. Res.* **31**, 69-78 (1991).
50. U.S. Environmental Protection Agency. 1990. National Contingency Product Schedule.
51. ExxonMobil Biomedical Sciences, Inc. 1999. Project No. 142060. Clinton, New Jersey. Unpublished data.
52. F. M. Mitchell and D. A. Holdway. 2000. The acute and chronic toxicity of the dispersants Corexit 9527 and 9500, water accommodated fraction (WAF) of crude oil, and dispersant enhanced WAF (DEWAF) to *Hydra viridissima* (green hydra). *Water Research* 34:343-348.
53. I. Gulec and D. A. Holdway. 2000. Toxicity of crude oil and dispersed crude oil to ghost shrimp *Palaemon serenus* and larvae of Australian Bass *Macquaria novemaculeata*. *Environmental Toxicology* 15:91-98.
54. Mervin Fingas, personal communication, March 6, 2003. Environment Canada.
55. J. Rodriguez-Grau, J. A. Schiazza, C. Villoria, G. Belisario, I. Galindo, R. Perez and L. Torres. 1995. Venezuelan oil spill national contingency plan: dispersant laboratory program. *Proceedings 1995 International Oil Spill Conference*, American Petroleum Institute, pp. 997-998. Washington, D. C. (1995).
56. S. L. Rhoton. 1999. Acute toxicity of the oil dispersant Corexit 9500, and fresh and weathered Alaska North Slope crude oil to the Alaskan Tanner Crab (*C. bairdi*), two standard test species, and *V. fischeri* (Microtox[®] assay). Master of Science Thesis. University of Alaska Fairbanks. 187 pp.
57. Dasic International. 2003. Personal Communication

ExxonMobil Oil Spill Dispersant Guidelines

58. M. I. El Samra, A. M. Abdallah and T. O. Said. 1995. Investigation on toxicity of crude oil and some oil dispersants to shrimp (Penaeus semisulcatus) and to Mugil Sehel fish of the Suez Bay. Journal of Environmental Sciences 9:105-114.

ExxonMobil Oil Spill Dispersant Guidelines

Appendix D AMOP References Dealing With Cold-Water Dispersion

(Unless otherwise noted, all references are from the **Proceedings of the Arctic and Marine OilSpill Program Technical Seminars**)

Belore, R.C. 2002. "Wave Tank Tests to Determine the Effectiveness of Corexit 9500 Dispersant on Hibernia Crude Oil Under Cold Water Conditions." No. 25b.

Blackall, P.J. and G.A. Sergy. 1983. "BIOS Project – Preliminary Results." No. 6.

Brandvik, P.J., M.Q. Moldestad, and P.S. Daling. 1992. "Laboratory Testing of Dispersants Under Arctic Conditions." No. 15.

Brandvik, P.J., T. Lunel, P.S. Daling, and A. Lewis. 1995. "Measurement of Dispersed Oil Concentrations by In-Situ UV Fluorescence During the Norwegian Experimental Oil Spill 1994 With Sture Blend." No. 18a.

Brown, H.M., R.H. Goodman, and G.P. Canevari. 1985. "Dispersant Effectiveness in Cold Water." No.8.

Brown, H.M., N.M. To, and R.H. Goodman. 1986. "Experimental and Theoretical Basin Studies of Dispersant Effectiveness in Cold Water." No.9.

Brown, H.M. and R.H. Goodman. 1988. "Dispersant Testing in a Wave Basin – Four Years of Experience." No. 11.

Brown, H.M. and R.H. Goodman. 1996. "The Use of Dispersants in Broken Ice." No. 19a.

Byford, D.C. 1982. "The Development of Dispersants for Application at Low Temperatures." No. 5.

Byford, D.C., P.J. Green, and A. Lewis. 1983. "Factors Influencing the Performance and Selection of Low-Temperature Dispersants." No. 6.

Byford, D.C., P.R. Laskey, and A. Lewis. 1984. "Effects of Low Temperature and Varying Energy Input on the Droplet Size Distribution of Oils Treated With Dispersants." No. 7.

Cox, J.C. and L.A. Schultz. 1981. "Dispersant Effectiveness Under Arctic Conditions, Including Ice." No. 4.

ExxonMobil Oil Spill Dispersant Guidelines

Daling, P.S. 1988. "A Study of the Chemical Dispersability of Fresh and Weathered Crude Oils." No. 11.

Farmwald, J.W. and W.G. Nelson. 1982. "Dispersion Characteristics and Flammability of Oil Under Low Ambient Temperature Conditions." No. 5.

Fingas, M.F., K.A. Highes, and M.A Schweitzer. 1987. "Dispersant Testing at the Environmental Emergencies Technology Division." No. 10.

Fingas, M.F., B.Kolokowski, and E.J.Tennyson. 1990. " Study of Oil Spill Dispersants – Effectiveness and Physical Studies." No. 13.

Lewis, A., Daling, P.S., T. Strom-Kristiansen, and P.J. Brandvik. 1995. "The Behavior of Sture Blend Crude Oil Spilled at Sea and Treated With Dispersant." No. 18a.

Mackay, D. 1995. "Effectiveness of Chemical Dispersants Under Breaking Wave Conditions." **The Use of Chemicals in Oil Spill Response**, ASTM STP 1252, P. Lane, ed., ASTM, Philadelphia, Pennsylvania.

Mackay, D., A. Chau, and Y.C. Poon. 1985. "A Study of the Mechanism of Chemical Dispersion of Oil Spills." **Environment Canada Report**. Ottawa, Ontario.

Mackay, D., R. Mascarenhas, K. Hassain, and T. McGee. 1980. "The Effectiveness of Chemical Dispersant at Low Temperature and in the Presence of Ice." No. 3.

Mackay, D and P.G. Wells. 1981. "The Use of Dispersants for Oil Spill Treatment." No. 4.

Mackay, D. and P.G. Wells. 1982. Recent Advances in Chemical Dispersion of Oil Spills." No. 5.

Nes, H. and S. Norland. 1983. "Effectiveness and Toxicity of Oil Dispersants." No. 6.

Sveum, P. 1987. "Fate and Effects of Dispersed and Non-Dispersed Oil in Arctic Mud Flats." No. 10.

Swiss, J.J., M. Vanderkooy, R.H. Goodman, and H.M. Brown. 1987. "Beaufort Sea Oil Spill Dispersant Trial." No.10.

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Appendix E Checklists for Dispersant Application

General Considerations

1.	What is the nature of the oil and is it likely to be dispersible?
2.	Is the spilled oil in an area where dispersants are approved for use?
3.	What is the most probable volume of spilled oil?
4.	Is there adequate dispersant supply available on hand?
5.	Is there an approved plan for this area?
6.	Does it specify conditions for dispersant use
7.	What are the local government requirements for applying for permission to spray dispersants?

Equipment

8.	Is the plan to use boats or aircraft for spraying?
9.	What equipment is available?
10.	Is it adequate for the operation proposed under the existing weather and sea conditions?
11.	Is the equipment on-site or nearby?

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12.	If not nearby, how soon can it arrive on site?
13.	Is the equipment reliable, properly designed, calibrated, and capable of applying dispersant at the desired dosage?
14.	Are application requirements consistent with the capabilities of the equipment?
15.	Can the supply be maintained to satisfy the timing demands of the spray program?
16.	Are trucks, forklifts, drum dollies, pumps, tools, and other support equipment available?
17.	Is there sufficient staff at the base of operations?
18.	Are the response authorities knowledgeable about the use and application of the chemical, or have they arranged to consult with someone who is?
19.	Have dosage calculations been made for the spray units available?
20.	Are adequate aerial guidance units and competent observers available?
21.	Are these aircraft equipped for the observer's direct radio contact with the application unit (boat or aircraft)?

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22.	Overall, considering the spill size and location, the distance from a base of operations and supply, dispersant availability, swath of the application equipment, chemical carrying capacity, speed of the application system, and the requirements of the spray treatment program, it is reasonable to assume that the proposed operation can be carried out with the equipment available in the time desired?
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23.	Have provisions been made for complete record-keeping regarding the dispersant application operation?
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Dispersant Application from Aircraft

24.	Are helicopters or airplanes to be used?
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25.	Are the required fuels and lubricants available?
-----	--

26.	What volume of dispersant can be carried per flight?
-----	--

27.	Will this be limited by the distance and time required per sortie?
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28.	What is the ETA of equipment to the staging area?
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29.	Are the proposed altitude and speed appropriate for ensuring low drift and high depositional accuracy with this dispersant?
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30.	If a bucket unit will be used on a helicopter, is it mounted close enough to the fuselage so that the pilot can see the ends of the spray booms in flight?
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31.	Is adequate ground support (equipment and personnel) available to allow rapid loading and refueling?
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32.	Does the airborne system have positive control of dispersant flow via a flowmeter or calibrated pump?
33.	Can the pump be turned on remotely?
34.	Are all nozzles directed aft?
35.	If not, can they be easily changed?
36.	Have calculations been made to determine operating conditions for the dosage desired?
37.	Is the required flow rate limited by the nozzle type used?
38.	For ground speeds of less than 100 knots, are the nozzle orifices used no smaller than D10-46 (<i>diameter = 0.156 in, 0.39 cm</i>)?
39.	For ground speeds greater than 100 knots, are the nozzle orifices appropriately sized for the pump rate required and shear regime limitations?
40.	Are nozzles of alternate sizes readily available?
41.	Can discharge pressure be controlled?
42.	Have provisions been made for capping or removing nozzles in order to meet dosage or Differential velocity requirements as necessary?

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Dispersant Application from Workboats

43.	Are any modifications necessary or desirable in booms, pumps, nozzles, or eductors, and can these be done, or parts obtained, without undue delay? For instance, is there a positive measurement or metering of the dispersant?
44.	Will the pump volume and pressure and the individual nozzles allow for production of a stable spray pattern at the dosage and operating speed desired?
45.	Are there any gaps between individual spray patterns at the water level?
46.	If needed, can necessary calibrations be made easily and rapidly?
47.	What area can be sprayed at the desired dosage by a single boat per unit time?
48.	Are other adequate boats and spray units available, if needed?
49.	Will spray boats suffice to control the spill, or will aerial application be necessary?

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