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Dispersant Studies of the Deepwater Horizon Oil Spill Response

Volume 1

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1.0 Introduction

1.1 Background

Beginning April 30, 2010, crews of the Deepwater Horizon Oil Spill Response operations tested a new technique to break up the oil before it reached the surface. Crews used a remotely operated underwater vehicle to inject the dispersant Corexit EC9500A directly into the escaping oil at the source. BP and the National Oceanic and Atmospheric Administration (NOAA) evaluated the results and concluded that it was feasible and highly effective.

On May 10, 2010, the Environmental Protection Agency (EPA) directed BP to implement their approved Dispersed Plume Characterization Plan for Subsurface Dispersant Application (the Plan; Appendix A). The Plan required BP to 1) prove that subsurface dispersant operation was successful at dispersing the oil plume undersea; 2) conduct a sampling regime to detect and delineate the dispersed oil plume; and 3) outline the operational procedures under which the subsea dispersant application would occur. These operational procedures indicated the type of dispersant to be used, the rate of dispersant injection, and the procedures for monitoring the operation.

On May 20, 2010, the EPA issued Addendum 2, which required BP to identify within 24 hours one or more alternative dispersants from the National Contingency Plan (NCP) Product Schedule that:

- were available in sufficient quantities;
- are as effective at dispersing the plume; and
- have a toxicity value less than or equal to 23.00 ppm LC50 toxicity value for Mendidia or 18.00 ppm LC50 for Mysidopsis, as indicated on the NCP Product Schedule.

Addendum 2 also required that BP immediately use only the approved alternative dispersant within 72 hours of receipt of the addendum.

As indicated in the BP response to the EPA, BP determined that the existing product, Corexit EC9500A, continued to be the best choice among dispersant products when considering toxicity, availability, and effectiveness at dispersing the oil plume.

- Only five products on the NCP Product Schedule met the toxicity criteria in the May 20th addendum.
- Of those five products, only Sea Brat #4 and Corexit EC9500A were available immediately and in sufficient quantities to be implemented within 72 hours (the timeline required under Addendum 2).
- Sea Brat #4 also appeared to be equally effective at dispersing oil.

Then BP considered one criterion in addition to the data available on the NCP datasheet – the potential for longer-term effects and persistence of the chemicals in each dispersant. Given the large amount of dispersant required and the proposed application near the ocean floor, this concern was particularly relevant. Sea Brat #4 contains a small amount of a chemical that may degrade to a nonylphenol (NP).

Various government agencies have identified this class of NP chemicals as potential endocrine disruptors that may persist in the environment for years (Appendix B). According to the UK Environment Agency,

> *NPE is very toxic to fish and other water dwelling organisms and is considered a hormone disrupting substance, mimicking estrogen. It degrades relatively readily in the environment to form the even more harmful nonylphenol (NP). Nonylphenol is not readily biodegradable and take months or even longer to degrade in surface waters or in soils and sediments... Bioconcentration and bioaccumulation [are] significant in water dwelling organisms and birds, where it has been found in internal organs at between 10 and 1000 times greater than the surrounding environment* (Appendix B).

By contrast Corexit EC9500A does not contain chemicals that degrade to NP. The manufacturer indicates that Corexit EC9500A reaches its maximum biodegradability within twenty-eight days of application, and that it does not persist in the environment. For those reasons, BP reported to the EPA that Corexit EC9500A appeared to remain the best choice when considering toxicity, efficacy, and availability within the timeframe required by Addendum 2.

In Addendum 3 to the Plan, the EPA directed BP to reduce its use of dispersants by 75% and to limit its volume of subsurface application to not more than 15,000 gallons in a single calendar day.

The Plan, its Addenda, and BP's response to Addendum 2 are presented in Appendix A.

1.2 Purpose

Prior to the issuance of Addendum 2 and BP's response letter, the BP environmental team had already 1) conducted a series of studies that compared effectiveness of alternative dispersants on the Mississippi Canyon 252 (MC 252) crude using lab Exdet tests, and 2) conducted field tests for four alternatives to the Corexit EC9500A product. Additionally, 3) the BP team obtained business-proprietary data (the chemical formulae) for all alternative products in order to consider the toxicity of ingredients that comprise the alternatives.

Subsequent discussions between EPA and the BP resulted in BP's commitment to continue searching for an alternative dispersant that was effective, available in sufficient quantities, and – most importantly – was less toxic. As a result, the BP team designed a series of efficacy and toxicity tests on the five alternative dispersants that meet the toxicity standards set out in Addendum 2 (as well as the Corexit EC9500A product currently in use). The commitment also included conducting a scientific literature review, and minimizing dispersant use, as well as presenting to the EPA the results of its previous studies.

The results of these previous studies are presented in this document, Volume 1. Section 2 presents a review of the existing literature on case studies concerning dispersant use in actual spill situations. Section 3 presents the lab Exdet effectiveness test results on the MC 252 sample crude, as well as the field effectiveness tests of alternative dispersants. Additionally, Section 3 presents a discussion of general results of toxicity comparisons based on formulae of the alternative dispersants under consideration. Section 4 provides a summary and recommendations resulting from the BP team's previously conducted studies and the literature review, and proposes the study protocols for a series of ongoing studies in effectiveness and toxicity testing on the five alternative dispersants that meet the

toxicity standards set out in Addendum 2 (as well as the Corexit EC9500A product currently in use) that will comprise Volume 2 (forthcoming). Volume 2 will include the results of these ongoing studies.

1.3 Contributors

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This document was prepared in collaboration with Arden Ahnell, Jim Barratt, Mark Fraker, and Al Maki.

1.4 Limitations

This report contains the working group's review of available data and published studies regarding dispersant use. It is intended to help the guide the company and agencies in choosing dispersants for further use in the MC 252 incident. The effectiveness and potential environmental effects of any dispersant used at this site has been, and will continue to be, the subject of additional study, data collection, analysis and further expert evaluation.

2.0 Review of the Scientific Literature on Actual Case Studies of Dispersant Use

2.1 Introduction

The use of oil spill dispersants at large oil spills has been infrequent. Large oil spills are rare and dispersant use has not always been feasible or desirable. Some of the largest oil spills in recent years (from the *Erika* in 1999 and *Prestige* in 2002) have been of very heavy fuel oil where dispersants would not have been effective. In other cases, such as the *Exxon Valdez*, the use of dispersants was considered and tried, but not implemented on a large scale. In other parts of the world, the use of dispersants on small oil spills is more frequent, but generally undocumented.

Data on dispersant use at real oil spills is sparse. None of the approved dispersant products from the NCP Product Schedule[1] have been used in quantity at large oil spills where their effectiveness and environmental impact have been well-studied. This limited information from real oil spills has often been supplemented by laboratory tests of dispersant effectiveness, or the toxicity of dispersant or dispersed oil. Owing to the small-scale and controlled laboratory conditions, the results are subject to misinterpretation.

The following sections present a review of the available scientific literature regarding the actual use of dispersants at oil spills and an assessment of their effectiveness and environmental impact.

2.2 Dispersants Overview

The aim of using dispersants is to transfer spilled oil from the sea surface into the water column in the form of very small oil droplets that will be suspended in the water column. The basic principles are described in the following paragraphs.

2.2.1 Natural Dispersion

To some degree, dispersion occurs naturally after an oil spill without dispersants, particularly if the sea is rough or the release occurs at depth. Breaking waves passing through an oil slick will convert the oil into droplets ranging widely in size. Most will be relatively large and will rapidly float back to the sea surface. Almost all crude oils float because their density is less than that of seawater. The rise velocity – the speed at which oil droplets will float back to the water's surface – is related to the size of the oil droplets; small droplets rise more slowly than large oil droplets. A small proportion of the droplets formed will be retained in the water column, depending on the wave energy.

2.2.2 Using Oil Spill Dispersants

Dispersants supplement natural dispersion. When sprayed onto spilled oil on the sea surface, dispersants soak into the spilled oil and the surfactants reduce the interfacial tension between the oil and the water surface. The oil/water interfacial tension (or surface free energy) is the property that inhibits the mixing of water and oil. When subjected to the energy of breaking waves, a higher

[1] Approved dispersants from the NCP Product Schedule include: Biodispers, Corexit® EC9500A, Corexit® EC9527A, Dispersit SPC 1000™, Finasol OSR 52, JD-109, JD-2000, Mare Clean 200, Neos AB3000, Nokomis 3-AA, Nokomis 3-F4, Saf-ron Gold, Sea Brat #4, and ZI-400.

proportion of dispersant-treated oil forms very small oil droplets, which are coated with surfactant molecules. These very small droplets, 20 to 100 μm diameters (individual oil droplets only just visible to the naked eye), have a very slow rise velocity through the water and tend to remain suspended in the water column due to the mixing energy of waves and currents (Cormack, D. and J. A. Nichols 1977).

The oil droplets are not created en masse after the application of dispersant. Addition of the chemical dispersant provides the potential for dispersion, but physical dispersion occurs only as a product of breaking waves, currents, and other movement through water. In other words, the dispersant weakens the oil's tendency to stay together, allowing the movement of the water to break it up. This results in temporary and transient dispersed oil plumes (or 'clouds') in the water column[2]. The oil does not disappear, but is rapidly diluted to very low concentrations.

The high surface-to-volume ratio of these tiny oil droplets facilitates 1) the loss and dilution of water soluble hydrocarbons and 2) the rapid colonization on the droplet's surface by hydrocarbon-degrading bacteria.

2.3 Concerns about Dispersant Use

2.3.1 Potential Effects of Dispersed Oil to Marine Organisms

Concerns about using dispersants often revolve around a central point: dispersing the oil exposes some marine organisms to more-elevated concentrations of hydrocarbons than would have occurred had dispersants not been used. Specifically,

- The slightly water-soluble (and potentially acutely toxic) oil components (i.e. Benzene, Toluene, Ethylbenzenes, and Xylenes) will be released more rapidly.
- The dispersed oil droplets may also contain low levels of chronically toxic and potentially carcinogenic PAHs (Polycyclic Aromatic Hydrocarbons) (Hellou, J. 1994 and 1996).
- The dispersed oil may become more available to filter-feeding zooplankton (Franklin, F. L and R. Lloyd 1982).

These concerns need to be addressed, but the difference in exposure of marine organisms to potentially toxic hydrocarbons from oil that is chemically dispersed versus naturally dispersed will be a matter of degree. Light crudes disperse more readily that do heavy crudes. The natural dispersion at the North Cape diesel spill (French, 1998a and 1998b) compared to that of *Gullfaks* crude oil from the *Braer* (described in detail later in this section) are very pertinent cases. Both occurred in very rough seas. No dispersant was used at the North Cape spill and only a limited quantity was used at the *Braer* incident. Natural dispersion occurred to a very high degree at both incidents. The ecological effects of the natural dispersion of oil were studied in both cases.

The transport, fate, and potential effects caused by petroleum hydrocarbons are not simple. Some of the most acutely toxic are the so-called BTEX compounds (Benzene, Toluene, Ethylbenzenes and

[2] This process can be seen with the subsea application of dispersant in the current spill. When dispersants are applied at the wellhead, nearly 1 mile below the water surface, the oil appears to shoot up towards the surface and to start dispersing before it reaches the surface, as a result of the physical energy of ocean currents.

Xylenes). [3]In addition to being slightly water soluble, these compounds are highly volatile and will evaporate almost completely within 12 hours. Any assessment of the potential effects of dispersed oil needs to account for the rapid weathering (loss of volatile components and incorporation of water droplets) of the spilled oil prior to dispersant treatment.

Another factor is that marine organisms differ in their sensitivity to exposure to water-soluble compounds and dispersed oil. Some are very robust, while others, particularly some early life-stages, are highly sensitive to pollutants, including oil. Mobile species, such as finfish may move away from oil-contaminated areas.

Toxicity testing needs to be conducted under an exposure regime that is relevant to the use of dispersants at sea. A lot of the toxicological studies in the past have used inappropriate exposure regimes. A standard toxicity assessment technique used to be the LC50 (lethal concentration 50) protocol, where the test organisms were exposed to a range of concentrations of the pollutant for a specified period (48 hours or 96 hours). The concentration resulting in a 50% mortality (LC50) guided the assessment. This sort of testing cannot represent the potential effects of chemically dispersed oil. Despite this, many such studies have been conducted in the past, resulting in misleading information.

The mixing energy of waves and currents transports these small, chemically dispersed droplets throughout the water column, distributing them laterally and vertically. This process continually dilutes the concentration of oil droplets and the soluble hydrocarbons in the water column, thus decreasing the concentration to which aquatic organisms are exposed. The exposure of marine organisms to high concentrations of dispersed oil is localized and brief, depending on the particular circumstances. Field measurements of hydrocarbon concentrations are typically less than 1 ppm (parts per million) within a few hours.

The concerns surrounding dispersant use must be balanced against the serious impacts that can result from allowing the spilled oil to remain on the sea surface, where it often drifts ashore to contaminate sensitive habitats such as marshes and wetlands. The consequences of oil pollution in such sensitive habitats can be long-lasting and severe.

2.3.2 Public Concerns about Dispersant Use

Several factors can combine in the public mind to produce unease or concern about the use of dispersants at oil spills:

- Oil spill dispersants are chemicals.
- The precise composition of the different dispersant formulations is proprietary and, although it may be disclosed to relevant government agencies for evaluation, it is not available to the public for commercial reasons.

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[3] "BTEX compounds are acutely toxic to aquatic organisms if contact is maintained. BTEX compounds are relatively soluble in water... BTEX are generally neurotoxic to target organisms. Benzene, in particular, has also been found to be carcinogenic to mammals and humans" (excerpt from abstract from *Oil in the Sea III: Inputs, Fates, and Effects* authored by the Committee on Oil in the Sea: Inputs, Fates, and Effects, National Research Council; obtained at National Academies Press website: http://www.nap.edu/catalog.

- As discussed below, oil spill dispersants are – throughout the world – subjected to toxicity tests to ensure that they do not pose an unacceptable level of adverse impact to the environment.

Although proprietary, the surfactants and solvents in oil spill dispersants are not manufactured solely for use in this application. Various chemical companies manufacture a broad range of surfactants for sale to other companies that formulate dispersants by blending different surfactants with solvents and other materials to produce the final product. All of the surfactants in oil spill dispersants are used in some other products, including household detergents and commercial and industrial cleaners.

Following concerns raised after the dispersant response to the 1993 *Braer* oil spill, the types of surfactants and solvents used in different types of dispersants were described in the 1994 MAFF (Ministry of Agriculture, Fisheries and Food, a UK government department since merged into the DEFRA [Department for Environment, Food and Rural Affairs]) review of The UK Oil Dispersant Testing and Approval Scheme. The EMSA (European Maritime Safety Agency) Manual on the Applicability of Oil Spill Dispersants (EMSA 2005, revised in 2009) contains a table based on Rycroft et al., 1994 (Table 2.1, below). The information presented in this table relates to oil spill dispersants that were approved for use in the UK in 1994 and may not necessarily be indicative of the surfactants and solvents used in dispersants on the current EPA NCP Product Schedule. However, it is most likely that any oil spill dispersants will contain some of the above surfactants and solvents or the near chemical analogues.

Table 2.1 Excerpt from EMSA Manual on the Applicability of Oil Spill Dispersants

Surfactants	*Solvents*
(i) Fatty acid esters (ii) Ethoxylated fatty acid esters	Light petroleum distillates: Odorless or de-aromatized kerosene Low aromatics (less than 3% wt.) kerosene CAS No. 64742-47-8 EC No. 265-149-8
(i) Fatty acid esters or sorbitan esters such as Span™ series CAS No.1338-43-8 (ii) Ethoxylated fatty acid esters (PEG esters) or ethoxylated sorbitan esters such as Tween™ series CAS No. 103991-30-6 (iii) Sodium di-iso-octyl sulphosuccinate EC No. 209-406-4 CAS No. 577-11-7	Glycol ethers such as: Ethylene glycol Dipropylene glycol 2-butoxyethanol (Butyl Cellosolve™) CAS No. 111-76-2 Di-propylene glycol monomethyl ether CAS No. 34590-94-8 EC No. 252-104-2 Light petroleum distillates: Hydrotreated light distillates CAS No 64742-47-8 EC No. 265-149-8

2.4 Dispersant Use at Oil Spills

Dispersants are not often used to counter large oil spills because: large oil spills are rare events; dispersant use is not always appropriate; and implementing a dispersant response requires the timely deployment of resources that may not be readily available. In some countries, particularly in the past,

the use of dispersants on small oil spills was an almost routine 'remedy.' An analysis of the available data on the frequency of dispersant use throughout the world (Steen and Findlay, 2008) and based on Etkin (1999), Henry (2005) and other sources, showed that dispersant use had been recorded on 213 occasions since 1968 (see Table 2.2). Dispersants were used most often in the period from 1988 to 1997 (mainly in south-east Asia) and the subsequent, less-frequent usage is thought to be related to the decline in the number of oil spill incidents from oil tankers.

Despite this relatively high number of usages of dispersants, the information available from these incidents is very sparse. Most applications were in response to small spills. The effectiveness of dispersant use was not determined by scientific methods and in most cases only subjective visual assessments were made; at 50% of the incidents the use was judged to have been "effective," at 24% it was judged to have been "ineffective," and at 24% of the incidents the results were either "unknown" or "inconclusive." In most cases, from the 1960s to the mid-1980s, there was little effort to assess the effectiveness of the response, let alone the effectiveness of the use of dispersant. Similarly, there was, usually little attempt to study the environmental impact. The low incidence during the period of 1998-2006 of a dispersant's being used and being found "ineffective" or "partially ineffective" (4 incidents; 12% of the total of 32 incidents for this period) indicates that, on a worldwide scale, the use of dispersants on oils that are known to be difficult to disperse is declining.

Table 2.2 Frequency of Oil Spill Dispersants Used Per Decade

Decade	*Number of Incidents at which Oil Spill Dispersants were Used*
1968 - 1977	42
1978 - 1987	47
1988 - 1997	86
1998 - 2007	38
Total	213

A similar study was conducted of response to marine oil spills over a 10-year period (1995–2005) (Chapman et al. 2007). They reviewed ITOPF's (International Tanker Owners Pollution Federation) database of past oil spills and found that, of the 258 marine incidents that the ITOPF was involved with between 1995 and 2005, 46 (18%) involved the use of oil spill dispersants at sea. Half of these took place in waters in south-east Asia. Thirty-nine percent of the dispersant applications were on heavy fuel oils, which are known to be poorly dispersible, and with many dispersant formulations. This may explain the apparently high incidence (38%; 34 incidents) of dispersant use being described as "ineffective." Of the 77 incidents in Europe during the period, 6 (8%) involved the use of dispersants at sea: one in France, one in Cyprus, two in Greece, and two in the UK.

There have been few oil spills in recent years where dispersants have been used:

- On 11 August 2006, the coastal tanker *Solar 1*, transporting 2,000 tons of oil, sank in waters 300 meters deep near the island of Guimaras in the Philippines. Over 1,300 tons of oil were spilled at sea very rapidly. The coast was heavily polluted by regular release of oil though leaks in the hull. Some dispersants were sprayed onto the main slick, but the effectiveness is not known. Adverse

weather conditions delayed response and probably reduced the effectiveness of the dispersants.

- On 18th January 2007, the container ship *MSC Napoli*, en route from Antwerp to Lisbon, was caught in a storm at the entry to the Channel and suffered structural damage to the hull. The vessel was beached off Branscombe, Devon, UK and a lengthy operation was mounted to remove the 2,318 containers and 3,500 tons of bunker fuel oil on board. A small amount (estimated as 9 tons) of IFO-380 oil was spilled on January 23rd and this was sprayed with 1 ton of dispersant. The spraying was judged to be successful.

- On 7th December 2007 the tanker *Hebei Spirit*, laden with 209,000 tons of crude oil, was struck by the crane barge *Samsung Nº 1* whilst at anchor about five miles off Taean on the west coast of the Republic of Korea. About 10,500 tons of crude oils (Iranian Heavy, Upper Zakum and Kuwait Export) crude oils were released into the sea. The oil polluted three of the four provinces along the western coast of the Republic of Korea. Dispersants were tested, but not used on a large scale in the response.

- On the morning of 12th December 2007, during oil offloading from the *Statfjord A* platform in the North Sea, about 4,300 cubic meters of crude oil was spilled into the sea from a sub-surface pipeline. The accident occurred when the tanker *Navion Britannia* was loading oil from a loading buoy. Dispersants were not used in the response and the oil dispersed naturally.

- On 16th February 2008 at 23:00, an oil spill occurred at the loading buoy of the FPSO Dalia (around 130 kilometers offshore Angola), during a transfer operation to a tanker. Dispersants were applied to the slick, but details are not available. Recovery operations then began at sea to recover oil that had not been dispersed. No oil came ashore.

2.4.1 Dispersant Use in US Waters

A paper by Charlie Henry at the 2005 IOSC (International Oil Spill Conference) – A Review of Dispersant Use in US Gulf of Mexico Waters Since the Oil Pollution Act (OPA 90) (Henry 2005) – described the occasions up until that time when dispersants had been used in Gulf of Mexico waters:

- West Cameron 198 Pipeline Spill, December 1995. 500 gallons of Corexit EC9527A sprayed from aircraft. No monitoring carried out.
- High Island pipeline System (HIPS) Oil Spill, January 1998. 3,000 gallons Corexit EC9527A sprayed. Aerial observations and water monitoring with fluorometer performed.
- T/V Red Seagull, January 1998. 2 barrels of Corexit EC9500A with fire monitor. Only visual observations made.
- Mississippi Canyon 109, Pipeline Spill, September 1998. 4,900 gallons of Corexit EC9527A and Corexit EC9500A sprayed from aircraft. Only visual observations made.
- M/V Blue Master, August 1999. 700 gallons of Corexit EC9500A sprayed from aircraft onto IFO-180 fuel oil. No water monitoring conducted.
- Poseidon Pipeline oil Spill, January 2000. 6,000 gallons of Corexit EC9527A sprayed from aircraft. Oil in water concentrations monitored with fluorometers.

- Main Pass 69 Pipeline Spill, September 2004. 5,000 gallons of Corexit EC9500A and 300 gallons of Corexit EC9527A used.

The author noted that:

> *What monitoring was conducted did meet the operational objectives, but contributed little to the science of dispersed oil. Spills are unplanned and uncontrolled events. Proper science requires proper controls that are inconsistent with an uncontrolled event. Studying dispersant effectiveness, fate and effects during an emergency spill response in the open sea environment is nearly impossible within acceptable scientific guidelines.*

2.4.2 Science and the Response to Oil Spills

From a historical perspective, the use of dispersants at many oil spills has not been studied scientifically. Other means, such as sea-trials, tank tests and laboratory studies have been used to assess effectiveness and the possible consequences of dispersant use. These are considered later in this report.

However, there have been two large spills and several smaller spils in relatively recent time where dispersants have been used, their effectiveness has been monitored, and the ecological consequences studied:

- The *Braer* spill in Shetland in 1993 where 84,000 tons of Gullfaks crude oil was naturally dispersed into the sea (although 120 tons of dispersant were spayed at the early stages of the incident, before most of the oil was released into the sea).

- The *Sea Empress* spill in Wales in 1996 where 72,000 tons of Forties crude oil was spilled in the sea and sprayed with just over 400 tons of dispersant.

2.4.2.1 *The Braer* spill in 1993

Summary of the Incident

On the morning of the 5th January, 1993, the oil tanker *Braer*, en route from Norway to Canada and laden with 84,700 tons of Gullfaks crude oil, ran aground at Garths Ness, a rocky promontory at the south of Shetland (an island north of Scotland). Crude oil began to escape from the vessel from the moment it grounded. Aerial surveillance was used to track the oil as it started to drift. Just over 100 tons of dispersant was sprayed onto the oil on January 6th, but the weather, already bad - the wind speed on January 5th was 35 knots with gusts up to 60 knots – deteriorated. Force 9 winds, gusting to Force 11 on January 8th, made dispersant spraying impossible. Ten-meter waves were reported around the wreck of the *Braer*. As the wreck started to be broken up by the waves, oil was released from the breached tanks. In a brief lull in the weather another 20 tons of dispersant were sprayed on January 9th when a very large release of oil was observed. The very high wind speeds (Force 11 - 12, gusting to 13 -14) and violent wave action continued for the next 3 days and the weather was bad for the next 3 weeks. Observations made from surveillance aircraft were used to track the drift of the oil on the sea. An underwater survey of the vessel was not possible until January 24th. That survey reported that the ship was completely broken up and no significant quantity of oil remained in the wreck. It became clear that the *Braer* had lost all of its crude oil cargo into the sea within a week of grounding.

Monitoring

Immediately following the grounding of the *Braer*, while oil was spilling from the wreck, the concentration of oil in the area close to the wreck was measured at some hundreds of parts per million (ppm) (Thomas, D. and T. Lunel 1993). In the days following the spill the waters around the wreck site exhibited oil concentrations as high as 50 ppm, but by ten days after the spill this had fallen to about 4 ppm and was down to background values in 30 - 40 days (Kingston, 2005). Gullfaks crude oil is a light crude oil with a very low asphaltene content; when 'weathered' it forms only a weakly stabilized water-in-oil emulsion. The 84,000 tons of crude oil was totally dispersed by the wave action in the extremely rough seas; the addition of 120 tons of dispersant (Dasic Slickgone LTSW, 95 tons; Dispolene 34S, 15 tons and 10 tons of Enersperse 1037) to some of the released oil probably had little, if any, effect because most of the oil was not on the surface of the sea, but had been naturally dispersed into it.

Impacts

The impact of the *Braer* oil spill was the subject of a large number of studies and the results have been summarized by Davies, J.M., A.D. McIntosh, R. Stagg, G. Topping and J. Rees 1997; Davies and Topping, 1995 and Kingston, P. 1999. Following the *Braer* spill in Shetland 1993, the ESGOSS committee (Ecological Steering Group on the Oil Spill in Shetland) (ESGOSS, 1994) oversaw the monitoring and environmental impact assessment. Impacts were:

Sea birds. The area affected by the *Braer* oil spill included feeding roosting and breeding grounds for many types of seabirds, but few are present in the mid-winter (Huebeck 1997). There were few observed mortalities. Monaghan et al., 1996 studied the potential sub-lethal effects of the spill on seabirds. They found no evidence of reduced breeding after the spill.

Fisheries. The fisheries were closed as soon as the incident occurred to avoid any risk of contaminated produce getting onto the market. During the first 3 weeks following the spill almost all species of fish and shellfish within the exclusion zone were found to contain elevated levels of PAHS (Topping et al., 1997). However, the concentrations of PAHs in fish caught within the area diminished rapidly and the fisheries were opened 2 months after the incident. There were 23 salmon farms within the exclusion zone. These fish could not swim away from the oil in the water and some became heavily contaminated with oil. Despite the very high levels of dispersed oil in the water, mortality levels were not unusually high. Because of tainting and the PAH level in the fish, they could not be sold. Concentrations of PAH within the salmon reached high levels, but declined rapidly after exposure. Because of the potential damage to the reputation of the salmon from this area, all the stocks of the 2 year classes affected were destroyed even though analysis indicated that only the occasional salmon was judged to be tainted (Howgate, P. 1987) (Goodlad, J. 1996).

Sand eels. Sand eels are important prey for many species of fish, seabirds, and marine mammals. The *Braer* spill occurred near to important sand eels grounds and both eels and their eggs were exposed to contamination (Wright et al. 1997). Monitoring showed no impact on the population of sand eels; the same high population densities were recorded the year after the spill as in the year before the spill.

Shellfish. Crabs, lobsters and bivalves within the fisheries exclusion zone rapidly accumulated very high concentrations of PAHs within their bodies (Topping et al., 1997). There was rapid depuration of contaminants from lobster, approaching background levels one month after the spill; the rate of loss of

PAHs from crabmeat was slower, approaching background levels after 12 months. The level of accumulation was highest in bivalves and the rate of depuration was initially high, but slowed only returning to background levels after 12 to 18 months. The Norway lobster *(Nethrops)* was most badly affected. Living in soft sediment, they were contaminated by naturally dispersed oil that had become trapped in the sediment as the ferocious wave conditions subsided. They continued to be contaminated for many years after the incident.

Impact and recovery on shoreline and sub-littoral habitats. Because the Gullfaks crude oil was naturally dispersed into the sea, there was no direct impact of oil on the shore. In the days during and immediately after the spill, large numbers of sub-tidal species were found washed up on the shore, including fish, sea urchin, razorfish and octopus. How much of this was due to the storm (strandings are common after severe storms) and how much was due to the dispersed oil is not clear.

Rocky Habitats. Despite the very high dispersed oil concentrations that had been in the water, there was no measurable impact from the spill in the rocky sub-tidal habitats (Kingston et al. 1997). There was an accumulation of oil in sediment further offshore at one location where a peak of oil contamination in excess of 10,000µg/g was found, but studies conducted over the following 2 years saw little change in the seabed communities.

Otters and Seals (Conroy, J.W.H., H. Kruuk, and A.J. Hall. 1997).

The conclusion of the ESGOSS (Ecological Steering Group on the Oil Spill in Shetland) (ESGOSS, 1994) was that:

> *Overall, the impact of the oil spill on the environment and ecology of South Shetland has been minimal. Adverse impacts did occur but were both localized and limited. The resilience of ecosystems and species populations has already been powerfully demonstrated and provides confidence and reassurance for the future.*

2.4.2.2 The *Sea Empress* spill in 1996

Summary of the Incident (MPCU 1996)

The tanker "*Sea Empress,*" transporting 130,000 tons of Forties crude oil, grounded at the entrance to Milford Haven in Wales, UK in February 1996, releasing 72,000 tons crude oil and 480 tons of heavy fuel oil into the waters of southwest Wales. The circumstances led to the release of 'fresh' crude oil, amenable to chemical dispersion, during each ebb tide, which was carried into deep water to the south of Milford Haven. This enabled the extensive dispersant spraying operation, which included the aerial application of 446 tons of dispersants to enhance the natural dispersion (Table 2.3). Several different dispersants were used (Table 2.4).

Monitoring

The movement of the spilled oil was tracked by aerial surveillance patrols several times each day. Monitoring of the dispersant spraying operations was carried out by UVF fluorometer measurements before and after dispersant spraying (Lunel et al., 1997.) The techniques and procedures were similar to those used in sea-trials in the North Sea, conducted before and after the *Sea Empress* incident (Lunel, T,

1995, Lunel et al., 1996, Lewis et al., 1998). Towed fluorometers set a different depths were towed along transects across areas of the oil to be treated with dispersant before spraying started and again after spraying by the aircraft had been completed.

Dispersant spraying was concentrated on freshly released crude oil. The water-in-oil concentrations were found to be 3 ppm at one-meter depth and less than 0.4 ppm at four-meter depth before dispersant spraying. After dispersant spraying, the water-in-oil concentrations were found to be 3 to 10 ppm at one-meter depth, 3 ppm at four-meter depth and 3 ppm at fifteen-meter depth (Lunel et al., 1997).

Dispersant was also sprayed onto oil that had emulsified. Monitoring measurements showed that the water-in-oil concentration was less than 1 ppm at 1 meter below dispersant spraying. This rose to 3 ppm at one meter, 1 to 3 ppm at four-meter depth and 1 ppm at fifteen-meter depth after dispersant spraying.

Table 2.3 Volume of Oil Spilled and Dispersant Sprayed at Sea Empress Spill

Date	*Oil spilled (tons)*	*Dispersant Sprayed (tons)*
Feb 15	2,000	0
Feb 16	-	2
Feb 17	5,000	2
Feb 18	7,000	29
Feb 19	28,000	57
Feb 20	15,000	110
Feb 21	15,000	179
Feb 22	-	0
Total	72,000	446

Table 2.4 Type and Amount of Dispersants Sprayed at Sea Empress Spill

Dispersants	*Amount used (tons)*
Corexit EC9500A	8
Enersperse 1583	14
Dasic Slickgone LTSW	97
Superdispersant 25	31
Dispolene 34S	31
Finasol OSR 51	212
Dasic Slickgone NS	53

UVF monitoring continued well after the oil had been dispersed to monitor the decrease in dispersed-oil-in-water concentration with time. It was found that the dispersed-oil-in-water concentration dropped from 10 ppm just after dispersant spraying to 1 ppm within 2 days, 0.5 ppm within one week, 0.2 ppm within one month and was at background levels after three months (Lunel et al. 1997).

Outcome of Response and Effectiveness of Dispersant

It is not possible to construct a 'mass balance' accounting of the amount or proportion of the oil dispersed from UV fluorometry measurements. The dispersed oil is distributed in scattered and rapidly dispersing plumes of dispersed oil formed by individual breaking waves under a dispersant-treated oil slick. It is not possible to have enough resolution in time (measure oil-in-water concentrations at all locations beneath the slick) or space (measure at a sufficient number of point or along transects to measure the local variations) to make such a mass-balance calculation.

Experiments conducted after the oil spill in controlled conditions at sea and in the laboratory allowed a committee of experts (SEEEC, 1998) to conclude that the probable mass balance of Forties Blend crude oil was:

- Approximately 40% (approximately 29,000 tons) evaporated from the oil soon after it was released from the vessel.
- Approximately 52% (approximately 37,000 tons) of oil was dispersed into the sea.
- Approximately 6% (approximately 4,000 tons) of oil, as 12,000 tons of water-in-oil emulsion) was recovered from along 200 km of the shoreline (Colcomb et al., 1997).
- Approximately 2% (approximately 1,500 tons) of oil was recovered at sea.

Further consideration of results from laboratory investigations allowed the committee to conclude that of the approximately 37,000 tons of oil dispersed into the sea, about 10,000 tons (with a range of 5,000 to 15,000 tons) would have been naturally dispersed into the sea and that 27,000 tons (with a range of 22,000 to 32,000 tons) was dispersed after being sprayed with dispersant. There is uncertainty in these figures, but they are best estimates.

These figures indicate that for each ton of dispersant sprayed from the aircraft, 40-80 tons of oil were dispersed. Such treatment rates were confirmed to be effective in subsequent laboratory tests.

If the 27,000 tons of oil that had been chemically dispersed had remained on the sea surface, it would have eventually been converted into approximately 100,000 tons of water-in-oil emulsion. Some of this emulsion would have drifted onto the shore where it would have caused significant damage (Lunel T., Rusin J., Bailey N., Halliwell C., and Davies L. 1997).

Environmental / Ecological Effects

The impact of the "*Sea Empress*" spill was extensively monitored directly after and in the years following the spill. The Environmental Impact of the *Sea Empress* Oil Spill - Final Report of the *Sea Empress* Environmental Evaluation Committee (SEEEC, 1998) (Edwards, R. and I. White 1999) was published in 1998. A summary report was published in 2004 (R.J. Law and C. Kelly 2004) and this paper included the findings of studies that had continued after the publication of the SEEEC Report. The following are the highlights of this scientific paper.

The coastline around south-west Wales is of exceptional conservation interest, and the area also supports a diverse fishery with extensive shellfish beds in some of the estuarine areas (Gray 1995; Pawson et al. 2002). Following the spill, a monitoring program for fish and shellfish in the area was initiated, and subsequently a fishery closure area was established as a precautionary measure. A

monitoring program was undertaken of the concentrations of both hydrocarbons and polycyclic aromatic hydrocarbons (PAH) in fish and shellfish tissues, and in edible seaweed (Moore, J., S. Evans, B. Bullimore, J. Hodges, R. Crump, J. Cremona, F. Bunker, D. Rostron, A. Little, Y. Chamberlain, P. Dyrynda and A. Worley 1997). Further details of the sampling program and the analytical methods used are given elsewhere (Kelly and Law 1998; Law et al. 1998). Hydrocarbon analyses in waters and surface sediment samples were also conducted to understand the movement and distribution of the spilled oil.

Effects on commercially exploited crustaceans and fish. (Law R. J. and C. A. Kelly 1999) and (Coates, P.J. 1998) There were no reports of mortalities of commercially exploited crustaceans or fish (including salmon and sea trout) as a result of the oil spill. Large numbers of dead or moribund shellfish (mostly bivalve mollusks) were washed ashore during the weeks following the spill (SEEEC 1998), although none of these involved the major commercial stocks. Other than within Milford Haven itself, hydrocarbon concentrations in crustaceans also remained low and, as in the case of finfish, low-molecular weight PAHs dominated. Within Milford Haven, total PAH concentrations within the range 100 to 2450 µg kg−1 were found in samples of edible crabs, velvet crabs and lobsters sampled in the period February to April, and occasional concentrations in the lower part of the range were still evident in May and June in samples from heavily impacted sites (such as in Angle Bay, and close to the mouth of Milford Haven). These concentrations declined rapidly, and total PAH concentrations in edible tissues were well below 100 µg kg^{-1} by the time restrictions were removed. As a prerequisite to lifting the closure order taint tests were conducted; no taint was detected, however, in samples of crabs and lobsters tested by the taste panel.

Hydrocarbons in both liver and muscle of all finfish, including migratory fish (salmon and sea trout) remained relatively low throughout the incident. The concentrations of PAH in salmon flesh (the summed concentrations of 19 individual PAH and groups (Σ PAH)) of 12 to 186 µg/kg wet weight) were much lower than those recorded following the *Braer* oil spill in Shetland in 1993, when concentrations of up to 14 000 µg/kg were found in caged salmon 10 days after the grounding (Whittle et al. 1997).

All the species of finfish sampled exhibited low concentrations of both hydrocarbons and PAH (Σ PAH values) <100 µg/kg wet weight in muscle tissue; (Law and Klungsøyr 2000), and, as they were not significantly elevated over those seen outside the affected area, it was not possible to observe any trend with time. In all cases fish took up primarily low-molecular weight PAH compounds (predominantly naphthalenes), presumably mainly from the dissolved phase by diffusion across gill surfaces. These compounds are more water soluble than the high-molecular weight PAHs (including those with carcinogenic potential), and so would have occurred at higher concentrations in the dissolved phase. Fish muscle generally contains only very low concentrations of PAHs as they have an effective mixed-function oxidase system that allows them to metabolize and excrete these compounds rapidly, and so the risk to consumers is minimized (Law and Hellou 1999).

Whelks sampled off Tenby on 25 February, when the first oil was beginning to come ashore in Carmarthen Bay, showed clear signs of contamination, with a total PAH concentration of 3800 µg/kg wet weight. This contamination seems to have been localized. From the beginning of June onwards, whelks taken across the whole area from Carmarthen Bay to the Isle of Lundy in the middle of the Bristol Channel yielded low concentrations, with all total PAH concentrations below 50 µg/kg. As for finfish and crustaceans low-molecular weight PAH predominated, and by this time no taint was evident.

The main commercial bivalve mollusk fisheries are for cockles and mussels in the Three Rivers and Burry Inlet areas off Carmarthen Bay, oysters (both native and Pacific) are reared at Carew (above Milford Haven), and scallops are also fished by boats from Milford Haven. All of these species were monitored routinely, and other species (e.g., clams, carpet shells, dog whelks, periwinkles, razor shells, trough shells) were analyzed either following stranding events, or to provide spatial coverage as available (Law R.J., Hellou J. 1999 and Fernley P.W., Moore M.N., Lowe D.M., Donkin P., Evans S. 2000). Hydrocarbon concentrations in both cockles and mussels exposed to oil rose rapidly and to high concentrations. At many of the sites within the closure area total PAH concentrations in mussels were well above 1000 µg/kg wet weight. The highest concentrations of PAHs in mussel tissues were seen at sites within Milford Haven close to the spill site, with total PAH concentrations >100 000 µg/kg wet weight being reached within about a week of the grounding. This reflected direct uptake of naturally dispersed oil droplets from the water column within a very short time after release from the vessel (Law et al. 1999). As the concentrations of oil-derived PAHs declined, a seasonal variation in the concentrations of the higher-MW, combustion-derived PAHs became apparent, and was particularly marked in mussels from within Milford Haven (Law, R. J., C. A. Kelly, K. L. Graham, R. J. Woodhead, P. E. J. Dyrynda and E. A. Dyrynda 1997). Concentrations of benzo[*a*]pyrene in mussels, in both 1996 and 1997, reached a maximum in March, declining to near zero in mid-summer. This seems to be related to larger combustion PAH inputs in winter, and to aspects of mussel physiology, which are discussed elsewhere (Law et al. 1999). Similar seasonal cycles in PAH concentrations in mussels have also been observed in both Germany and the Shetland Islands (Jacob et al. 1997; Webster et al. 1997).

The fishery restrictions were removed in stages as the results of the monitoring study (Kirby M.F., Neall P., Taylor T. 1999) showed that concentrations of hydrocarbons and PAHs had declined to levels that posed no risk to consumers, and that the species involved were free of taint (Lancaster J.E., Pawson M.G., Pickett G.D., Jennings S. 1998). These criteria were similar to those established after the *Braer* spill (Topping et al. 1997). Controls on fish and crustacea were removed 3 and 8 months, respectively, after the grounding), and the major intertidal cockle beds in the Burry Inlet and Three Rivers, which were lightly contaminated, reopened 4.5 and 7 months, respectively, after the grounding. The restrictions covering intertidal mussels in the south-east of the closure area and oysters within Milford Haven were the last to be lifted, remaining in place for about 19 months. Selective restrictions have remained in place for long periods following earlier spills, for instance, seven years for Norway lobsters (*Nephrops norvegicus*) and mussels off Shetland following the *Braer* oil spill in January 1993. This was a result of oil becoming entrained in subtidal sediments in the inner sounds and voes. Similar circumstances did not arise in the case of the *Sea Empress*, except around Skrinkle Haven and Caldey Island where oil persisted subtidally in sandy sediments until the end of 1996.

Studies of the seabed showed little impact resulting from the spill except for marked reductions in the abundance of amphipods (particularly *Ampelisca* spp, *Harpinia* spp, and Isaeidae) in some areas to the north of the grounding site (Levell et al. 1997; Rutt et al. 1998). Overall, the range of conspicuous species badly affected was very similar to those documented for two previous oil spills that occurred in the same general geographic area and with similar environmental conditions. Those spills involved the *Torrey Canyon* (Cornwall 1967) and the *Amoco Cadiz* (Brittany 1978).

Effects on plankton. Data from the routine surveys conducted using the continuous plankton recorder in the Bristol Channel and adjacent offshore areas indicated that the *Sea Empress* oil spill had no dramatic effects on the plankton of the southern Irish Sea between February and October 1996. All of the

common taxa showed normal levels of abundance, some taxa suggested in the literature to be susceptible to the effects of oil pollution showed no marked changes, and no striking changes were noted in the phytoplankton and zooplankton communities as a whole (Batten et al. 1998).

In the wake of the oil spill a number of biological effects techniques were deployed to assess exposure to PAHs and the likely occurrence of sub-lethal effects. These involved the determination of EROD (ethoxyresorufin-O-deethylase) in fish (Livingstone, D.R., Lemaire, P., Matthews, A., Peters, L., Bucke, D. and Law, R.J. 1993), measurements of immune function, scope for growth and lysosomal stability in mussels, DNA-adducts in fish and transplanted mussels and the application of whole-sediment bioassays to samples from within the Milford Haven waterway. These studies are reported in detail elsewhere (Dyrynda et al. 1997, 2000; Fernley et al. 2000; Kirby et al. 1999; Law et al. 1998; Lyons et al. 1997). A variety of impacts were observed, but all were short-lived.

The report concludes that:

> *The effects of the Sea Empress spill on fisheries were less severe than could have been expected on the basis of the quantity of oil spilt. There were no reports of mortalities of commercially-exploited crustaceans or fish (including salmon and sea trout) as a result of the oil spill. In* finfish *and crustaceans, the levels of contamination were low. This may have been partly due to the fact that the spring of 1996 was colder than usual, and feeding activity may have been reduced at the time the oil was released. Most of the crabs and fish may also have been offshore at the time of the spill due to the season. Much higher tissue concentrations were seen in bivalve mollusks, both from within and outside Milford Haven. Mass strandings of a number of species occurred, apparently as a direct result of the oil spill. Major stocks exploited commercially, such as those of the Three Rivers and the Burry Inlet, were not affected in this way. Biological effects studies likewise demonstrated a variety of impacts on local fish and mussels, but all were short-lived.*
>
> *There is little doubt that the aerial application of dispersants helped to reduce the impact of the Sea Empress spill on fisheries considerably by significantly reducing the amount of oil which reached the shoreline. It was estimated that the use of dispersants reduced the impact of the spill by preventing an additional 57000 to 110000 t of emulsified oil from impacting the beaches. Contamination by hydrocarbons and PAH persisted longest in mussels from the intertidal area to the east of Milford Haven (Freshwater West to Pendine Sands), and derived from bulk oil contamination of the shoreline. This is in line with observations at previous spills where contamination has persisted for years due to oil becoming trapped within sediments in low-energy coastal environments, resulting in recontamination when the oil is mobilized by storms or tides. The large-scale use of dispersants requires identification of the resources to be protected as part of a contingency plan and detailed (and rapid) consultation between government and nature conservation agencies before use, but can yield real environmental benefits.*

2.4.3 Conclusions from the Large-Scale Use of Dispersants at Real Oil Spills

Every oil spill has unique characteristics and circumstances that make it unlike any other. Consequently, information and experience gained at one spill response may not be directly transferable to other spills

and such information should be used with caution. However, the two spills described in this report are the only instances of major real-world dispersant use.

The two major spills at which dispersants were used in large quantities and which were the subject of extensive follow-up studies of the ecological effects were the *Braer* spill in 1993 and the *Sea Empress* spill in 1996. Both occurred in UK waters where the use of dispersants – in a pre-planned way and with at-sea monitoring and subsequent ecological studies – is incorporated into the National Contingency Plan.

These spills had some similarities:

- Both released large quantities of crude oil (84,700 tons from the *Braer* and 72,000 tons from the *Sea Empress*) from tankers that had run aground.
- Both occurred in areas with oil-sensitive resources and important fisheries.
- Both occurred in bad weather in the winter.
- Dispersants were applied in each case; approximately 120 tons at the *Braer* and 446 tons at the *Sea Empress*.

But there were dissimilarities as well:

- The crude oil spilled at the *Braer* incident, Gullfaks crude oil, was totally and naturally dispersed by the prevailing extremely rough sea conditions. The extremely bad weather with exceptionally high wind speeds persisted for a long period, which made active response actions difficult. The aircraft spraying dispersant at the start of the response were operating in extreme conditions, and therefore, it is unlikely than the dispersant altered the fate of the oil.
- The crude oil spilled at the *Sea Empress*, Forties Blend crude oil, was released sequentially on each tide and the prevailing wind took the oil offshore and into deeper water. This enabled an accurate and sustained dispersant spraying operation to be mounted over several days.

In both cases, a large proportion of the spilled oil was dispersed; dispersed naturally by the severe weather in the case of the *Braer*, with the assistance of dispersants in the less severe prevailing weather at the *Sea Empress* spill.

- Essentially all of the 84,700 tons of the Gullfaks crude oil spilled at the *Braer* spill was naturally dispersed into the water column in a few days. Water monitoring showed that the dispersed oil in water concentration rose to very high levels and then declined rapidly.
- Approximately 40% of the Forties Blend crude oil was judged to have evaporated before dispersant was sprayed onto the spilled oil. Hindsight analysis and post-spill studies indicated that approximately 52% (approximately 37,000 tons) of oil was dispersed into the sea. It was subsequently judged that approximately 10,000 tons would have been dispersed naturally and approximately 27,000 tons was dispersed as the result of dispersant spraying. These values were derived after extensive post-spill study and consideration.

There was comprehensive ecological monitoring after both incidents and the studies continued for several years. Many reports have been written on the various aspects considered (and are contained in the Reference list).

- In both cases, there were numerous ecological effects, as is inevitable at a large oil spill.
- The effects exerted by the large amount of dispersed oil (naturally dispersed in the case of the *Braer* and with assistance from dispersants in the case of the *Sea Empress*) were, in most cases, not severe and short-lived.
- Although there were strandings of large numbers of sub-tidal species in the days immediately after the spill at both incidents, there were only minor long-term effects (Levell, D. [Editor], Hobbs, G., Smith, J. & Law, R.J. 1997).
- Fish exposed to the dispersed oil had elevated levels of hydrocarbons within their tissues, but these levels dropped as the fish 'depurated' (excreted) the hydrocarbons back into cleaner water in the time after the incident.
- Commercial stocks of farmed salmon were deliberately destroyed at the *Braer* spill because of reputational issues, not because of high or persistent levels of hydrocarbon contamination.
- There were no observable effects caused by exposure to dispersed oil on the plankton populations at either incident.

The effect of the dispersant response at the *Sea Empress* spill and the combination of spilled oil type and ferocious weather conditions at the *Braer* spill that caused almost all of the spilled oil to be dispersed, were judged to have produced ecological effects that were much less severe than if the spilled oil had come ashore. This was the judgment made after extensive post-spill studies.

- It is obviously not possible to accurately quantify the differences in outcomes between something that did occur (dispersion of a lot of spilled oil at both incidents) with other things that did not occur; less severe weather conditions that could have prevailed (the *Braer* spill), or in the absence of a dispersant response at the *Sea Empress* spill.
- On the basis of the information and experience gained at both the *Braer* and *Sea Empress* oil spills, the UK Government has maintained the use of dispersants as a very active response option to major oil spills.

2.5 Assessing Dispersant Effectiveness

The phrase "dispersant effectiveness" has come to mean different things depending on the context.

Most simply, 'effectiveness' can mean a non-quantitative, subjective assessment. If spilled oil on the sea is sprayed with dispersant and then a light-brown plume of dispersed oil is easily visible in the water soon after a wave passes through the dispersant-treated oil, it is reasonable to say that the dispersant appears to be working well.

2.5.1 Dispersant Effectiveness in a Laboratory Test

"Dispersant effectiveness" can have a much more specific meaning when used to describe the results obtained from a specific laboratory test method. Dispersant effectiveness in this case is a numerical percentage value, where 0% is equivalent to no dispersion of oil at all and 100% is equivalent to total dispersion of all of the oil. A percentage value of dispersant effectiveness in this context is only strictly applicable to the test method, test oil, and the conditions (temperature, salinity, treatment rate etc.) under which it was obtained.

Many different dispersant test methods have been developed around the world (Clayton, J. R., J. R. Payne and J. S. Farlow 1993; Martinelli, F.N. 1984). In principle, they are all similar: dispersant is added to test oil on seawater (or is pre-mixed into it as in the case of the Swirling Flask Test (Blondina et al. 1997)) in a particular apparatus and the dispersant-treated oil and water are mixed by some agitation method (Bocard, C. and C. G. Castaing 1986). After a specified period, the mixing may be stopped and a sample of the water-oil-dispersant mixture is taken and analyzed. The methods differ in details, such as whether the dispersant is pre-mixed into the oil, the properties (viscosity, etc.) of the test oils, the intensity of agitation (Fingas, M., D. Kyle, and E. Tennyson 1993), and the relative volumes of oil and water (Desmarquest et al., 1985). Different methods produce different numerical results, even when the same dispersants and same oils are tested under otherwise identical conditions.

These small-scale tests are useful in ranking various products in terms of effectiveness, but do not accurately predict what will happen when dispersants are applied at sea (Delvigne, G. A. L. 1985).

It is important not to misinterpret the effectiveness value obtained in the laboratory directly into the likely performance at sea. A dispersant and test oil combination that produces a 60% result in the laboratory will not cause 60% of the volume of the same oil to be dispersed into sea, while leaving 40% of the oil volume on the sea surface. However, if dispersant A produces a dispersant effectiveness test result of 60% and dispersant B produces a result of only 30% with the same test oil, it is likely that dispersant A will perform 'better' at sea. This 'better' performance is most likely to manifest itself as more rapid dispersion of the oil, rather than 40% of oil being left on the surface when sprayed with dispersant A and 70% being left on the surface if sprayed with dispersant B.

Experience of dispersant performance gained in tank tests, at several sea-trials, and at actual incidents generally show that dispersant performance at sea is more sharply divided into (i) almost totally effective or (ii) almost totally ineffective, rather than a continuum from 0% to 100% dispersant effectiveness implied by the dispersant effectiveness results obtained in laboratory tests.

Laboratory systems do provide useful insights into the effectiveness of particular formulations on different oil types and weathering stages, as well as the effects of temperature. The bulk of information available on dispersant effectiveness in the technical literature has come from these small-scale laboratory tests.

More elaborate, 'meso-scale' tank tests and larger-scale wave basins have been used to gain better representations of dispersant effectiveness. Flume-like test tanks and wave basins also provide a convenient means to weather the oil on water to better represent actual spill-conditions at sea. Building such facilities and conducting experiments at these scales, however, is much more costly than simple lab experiments, but the results are likely to be more represent the actual physical and environmental complexities that influence dispersant effectiveness in the real world. Dispersant effectiveness can be quantified through analysis of water samples (using gravimetric, flourometric, or analytical chemistry techniques), particle monitoring, and mass balance approaches.

Full-scale field tests - or sea trials - are, of course, best for assessing dispersant performance but are very costly and difficult to carry out because of the complex logistics, and unpredictable weather (Daling, P. and R. Lichtenthaler, 1987). Additionally, large-scale tests with intentional releases of oil and dispersants into the environment are often met with complex permitting challenges in many countries.

2.5.2 Assessing Dispersant Effectiveness at Sea

Unfortunately, the simple, consistent and repeatable procedures used in laboratory tests cannot be duplicated at sea. The sea is an open system - not in a closed container - and dispersed oil is rapidly diluted to very low concentrations in a vast quantity of water. It is sometimes possible to know the exact amount of oil that has been spilled, but it is currently not possible to accurately measure the amount of oil that remains on the surface at any particular time, or to accurately measure the amount of oil that has been dispersed. It is therefore not possible to calculate the percentage of the original oil that has been dispersed and express this as a "dispersant effectiveness" value as can be so easily done in laboratory tests.

Dispersant effectiveness is commonly assessed using visual or photographic records. The action of dispersants is often visible as the formation of a light-brown plume, or 'cloud', of dispersed oil in the water column. While it can be fairly easy to observe dispersants working on some occasions, the viewing conditions can be more difficult on others. In poor visibility, it may not be possible to clearly observe dispersed oil in the water. Qualitative evidence of the dispersion of oil can be obtained by visual observation, but estimating the degree of dispersant effectiveness quantitatively at a real oil spill is much more difficult.

Field tests in various parts of the world have been conducted to identify the conditions under which dispersants work best. Since the 1980s, several well-documented field tests have been conducted in several countries, including Canada, France, Norway (Lichtenthaler, R.G and P.S. Daling 1985), (Lewis, A. 1995), (Brandvik et al., 1996) (Lewis, A., P. S. Daling, T Strøm-Kristiansen, and P. J. Brandvik. 1995), the USA (McAuliffe, C., B. Steelman, W. Leek, D. Fitzgerald, J. Ray, and C. D. Barker, 1981) and the UK (Lunel, T., 1994), (Lunel T., and L. Davies, 1996), (Lewis, A. A. Crosbie, L. Davies and T. Lunel, 1997). Fluorometry has been used to measure the dispersed oil concentrations in the water beneath and around test slicks (Law, R.J. 1984) (Law, R.J., Marchand, M., Dahlmann, G. and Fileman, T.W. 1987), and those that have been sprayed with dispersant (Hurford, N., Buchanan, I., Law, R.J. and Hudson, P.M. 1989). These comprehensive measurements, supplemented with sampling of surface and sub-surface oil and extensive use of remote sensing from aircraft, have allowed a quantitative estimate to be made of the amount of oil dispersed over time (Fiocco, R.J., P.S. Daling, G. Demarco and R.R. Lessard 1999).

The best method currently available for estimating the effectiveness of dispersant use at sea is Ultra-Violet Fluorometry (UVF) (Brandvik et al., 1995), such as is used in the SMART (**Special** Monitoring of Applied Response Technologies) monitoring protocol. UVF detects the aromatic components in oil. Submerged 'fish' are towed at several depths from 1 to 10 meters below an oil slick with the oil being pumped from this depth to a UVF instrument in a boat. The UVF instrument will detect the dispersed oil droplets and the partially water-soluble aromatic compounds that are released from the oil. The instrument needs to be calibrated for different types of oil and the calibration changes with the dilution of the dispersed oil as the oil 'weathers'. The UVF instrument readings can be 'back-calibrated' by taking water samples for subsequent analysis in a laboratory. This permits the relative concentration reading to be converted into absolute concentration readings such as ppm (parts per million) of dispersed oil in water. UVF readings taken below an oil slick before dispersant is used will record the dispersed oil concentrations in water that are produced by natural dispersion. If there is an obvious increase in the dispersed oil-in-water concentration below the dispersant-treated slick, compared to that underneath the untreated slick, this would indicate a high level of effectiveness, but the oil concentration values

along a line under the slick cannot be converted into a calculation of the total volume of oil dispersed from the slick. This is because the oil concentrations can only be measured along a 'transect' - a line across or along the slick - at a few water depths. To accurately calculate the total volume of oil dispersed at any particular time it would be necessary to measure the dispersed oil concentration at all points below the slick and this is not feasible with today's technology.

2.6 Assessing Toxicity of Dispersants and Dispersed Oil

There are many laboratory procedures for testing toxicity of dispersants, oil, and oil-dispersant mixtures to marine life (Doe, K. G. and P. G. Wells. 1978).

The standard 48-hour or 96-hour LC50 (Lethal Concentration for 50% of the test population) test is used for the approval of dispersants in some countries; it is a measure of the relative toxicity of different dispersants. The data are useful for discriminating between high and low toxicity products or mixtures, but cannot be used reliably for predicting environmental effects. This owes in part to the simplified and standardized experimental conditions used in laboratory tests and the different ways of assessing an organism's actual exposure to oil, dispersant, and dispersed-oil-water mixtures.

2.6.1 The Effects of Dispersant Alone or the Effects of Dispersed Oil?

Studies have shown that toxicity concerns should be focused on potential environmental effects of dispersed oil, rather than on dispersants themselves. Modern dispersants are used at low treatment rates (2 to 10% of the oil volume). Any potential toxicity of the dispersant alone is low in comparison to the toxicity of the much larger volumes of oil that are treated with dispersants. The potential effects of dispersed oil and dispersants are not synergistic; dispersants facilitate the creation of dispersed oil and therefore the potential of consequent effects, but do not – in themselves – contribute to these effects (Clark et al. 2001).

2.6.2 Test Oil

Because oil is a complex mixture of hydrocarbon compounds, particular components pose the greater toxic risks than others. These are generally hydrocarbons that are more soluble in water (Blackman, R.A.A. and Law, R.J. 1980) and that persist in the environment long enough to sustain exposures to aquatic organisms (Blenkinsopp, S. et al., 1997). Those components that rapidly volatilize, are not water soluble, or are rapidly degraded by microbes pose considerably less risk.

2.6.3 Test Species

Historically, LC50 toxicity testing has used a variety of species, sometimes - but not always - particularly sensitive species or the most sensitive life stages of representative or surrogate species as test organisms. This presents a very conservative approach to toxicity assessment, as many of the species and life stages exposed in the real world likely will be more tolerant. Lethality tests are not a particularly conservative basis for assessing potential impacts, as a focus on the health and reproduction of surviving animals is more comprehensive.

The ability of organisms to accumulate and metabolize various hydrocarbons varies greatly. Species with primitive metabolic systems often cannot breakdown hydrocarbons that enter their cells, making them

more vulnerable. Most vertebrate animals, and many of the more evolved invertebrates, have functional livers, or similar organs or cellular processes, which provide biochemical mechanisms that can breakdown accumulated hydrocarbons and remove them from their systems, although the biochemical breakdown products may have additional toxic effects. Survival, growth, and reproduction can be impaired by the presence of hydrocarbons or metabolites in the cells or tissues for long periods of time. Hydrocarbons can have reversible or irreversible effects on the nervous systems in higher organisms.

Environmental monitoring following actual spills in which dispersants have been applied point to little cause for concern about long-term effects, as plants, invertebrates and fish populations show little change in the short term and have recovered within months to a year.

2.6.4 Exposure Regime

The extended, constant exposure durations common in standard LC50 (48 or 96 hours) tests should be contrasted to the much shorter and rapidly diminishing exposures experienced by marine organisms when oil is dispersed in open waters. Significantly less than the expected toxicity from LC50 testing has been demonstrated in a number of laboratory studies that used environmentally realistic, rapidly decreasing exposure concentrations (Roubal, W. T., D. H. Bovee, T. K. Collier and S. I. Stranahan. 1977: Hyland, J. L., P. F. Rogerson and G. R. Gardner. 1977; Bragin, G.E., J.R. Clark and C.B. Pace. 1994; Carr et al., 1985; Bardot, C., and G. Castaing. 1987; Clark et al*.* 2001 and George-Ares, A. and J. R. Clark. 1997). Test procedures, such as the CROSERF protocols (Coelho, G.M. and D. Aurand [eds.] 1998), have been developed to better mimic environmentally realistic, short-term, declining exposures and have demonstrated that dispersed oil is up to 100 times less toxic compared to characterizations using standard LC50, continuous exposure test methods. Studies conducted in the field consistently show that aquatic animals are exposed to rapidly decreasing concentrations due to dilution effects from mixing by waves and currents, with initial concentrations of hydrocarbons reduced below laboratory effects levels within hours of dispersant application.

2.6.5 Lethality versus Sub-lethal Effects

More recent tests have investigated sub-lethal effects of dispersants and dispersed oil. These include assessing effects on animal and plant growth rates, reproduction, and general physiological and biochemical functions of healthy organisms. Reviews of published data on toxicity of oil and dispersed oil show a tremendous range in sensitivity among marine species (Lewis and Aurand 1997: Clark et al*.* 2001; NRC 1989; 2003; Markarian et al*.* 1993, and others). Investigators use different test methods, crude oils with different physical and chemical properties, test organisms at different life stages (ranging from eggs, larvae, juveniles to adults), and measures of toxic effects that range from acute mortality to subtle, non-lethal shifts in important cellular enzyme systems. Using information on sub-lethal impacts to understand the viability of exposed populations over the longer term is a significant research focus in contemporary environmental toxicology.

2.6.6 Past studies

Studies of the effects of dispersed oil have been conducted in the past on a wide range of organisms, species, and habitats (Table 2.5). Using this existing information about a very wide range of organisms presents the challenge of determining what information is relevant.

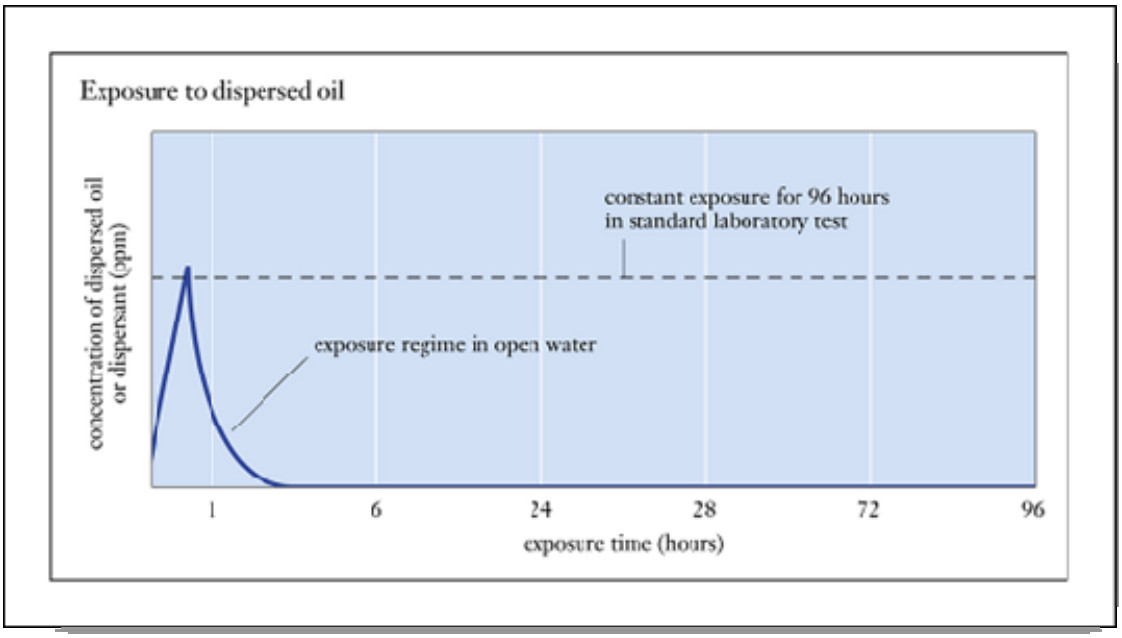

Figure 2.1 Exposure to Dispersed Oil

Table 2.5 Effect of Dispersant or Dispersed Oil in Various Studies

Study	*Effect of Dispersant or Dispersed Oil On*
Abbiss et al., 1981.	Sheltered intertidal habitats
Acreman et al., 1981.	An experimental marine ecosystem
Albers, P. H. and M. L. Gay. 1982	Breeding Ducks
Albers, P. H. 1979	Hatchability of Mallard Eggs
Anderson, J. W. 1986	Marine Invertebrates
Anderson, J. W. 1987	Shrimp and Fish
Anderson, J. W. et al., 1984	Marine Sediments
Anderson, J. W. et al., 1979	Benthic Amphipods
Anderson, J. W. et al., 1980	Marine Crustaceans
Anderson, J. W. et al., 1980	Clams
Anderson, J. W. et al., 1981	Shrimp
Anderson, M, A. et al.,1989	Jamaican Corals and Seagrass
Avolzi, R. J. and M. Nuwayhid 1974	Bivalves
Baca, B. J. and C. D. Getter 1984	Seagrass Thalassia testudinium
Baker, J. M. 1976	Splash zones
Baker et al., 1984	Variety of Intertidal Habitats
Baker et al., 1993	Salt Marshes
Ballou et al., 1987	Mangroves, Seagrasses, and Corals
Ballou et al., 1987	Tropical Marine Communities
Borseth et al.1986	Marine Fish Eggs

Table 2.5 (Continued): Effect of Dispersant or Dispersed Oil in Various Studies

Study	*Effect of Dispersant or Dispersed Oil on*
Carr, R. S. and O. Linden. 1984	Gammarus salinus and Mytilus Edulis
Chan, K-Y. and S. Y. Chiu. 1985	Chlorella salina
Cook, C. B. and A. H. Knap. 1983	Brain coral., Diplora strigosa
Crothers, J. H. 1983	Common animals and plants of rocky sea shores
Crowell, M. J. and P. A. Lane. 1988	Nova Scotia Saltmarsh
Depledge, M. H. 1984.	Carineus Maenas
Dodge et al., 1984, 1985a and b	Reef-building coral Diplora strigosa
Eastin, W. C. and B. A, Rattner 1982	Mallard ducklings
Englehardt et al., 1984	*Benthic invertebrates*
Englehardt et al., 1984	*Bivalves*
Fabregas, J. C. Herrero and M. Veiga 1984	*Marine Microalga Tetraselmis suecica*
Farke, H and others 1984, 1985	*Intertidal Ecosystem*
Foy, M. G. 1982	*Arctic marine fish and invertebrates*
Fuller, C.F. and J.S. Bonner. 2001	*Texas marine species*
Getter, C. D. and T. G. Ballou. 1983, 1985	*Mangroves*
Gulec, I. B. Leonard and D. Holdway. 1997	Amphipods and snails
Hartwick et al.1979	Littleneck clam Protothaca staminea
Howard, S. J. M. Baker & K. Hisock. 1989	Seagrasses
Hutcheson, M. and G. W. Harris. 1982	Arctic Bivalves
Knap, A. H et al., 1983, 1985 and 1987.	Brain coral Diploria Strigosa
Lai, H. C. and M. C. Feng. 1985	Mangroves
Lane et al., 1987	North-Western Atlantic Salt Marsh
LeGore et al., 1983	Arabian Gulf Corals
Levell, D. 1976	lugworm, Arenicola marina
Linden, O. 1974	Baltic Herring
Linden, O. 1975	Larvae of the Baltic Herring
Linden, et al., 1985	Littoral Ecosystem of the Baltic Sea
Linden, et al., 1987	An enclosed marine ecosystem
McKeown, B. A. 1981	Juvenile Coho salmon., Oncorhyncus kisutch
Ordzie, C. J. and G. C. Garofalo. 1981	Bay scallops Argopecten irradians
Rhoton etal., 2001	A cold-weather species
Teas. H. J. and E. O. Duerr. 1987	Rhizophora mangroves
Thorhaug, A. and J. H. Marcus. 1987	Subtropical / Tropical Seagrasses
Van Vleet, E.S. and D.L. Wetzel. 1997	Marine Organisms of Florida
Wetzel. D.L. and E. S. Van Fleet. 2001	A 3-year Florida study

2.6.7 Assessing the Risks of Dispersant Use

The concept of ERA (Ecological Risk Assessment) has been applied to decisions about oil spill response (Kraly et al., 2001) and dispersant use at oil spill response (API, 1999). Such a risk assessment

aims to put all the available information into a perspective that is accessible to all those that will be involved (the stakeholders).

It is possible to use the available information on hydrocarbon toxicity and expected environmental exposure duration (based on dilution rates) to select exposure concentrations associated with high, medium, or low risks for aquatic organisms (Pond, R.G, J.H. Kucklick, A.H. Walker, A. Bostrom, P. Fischbeck, and D. Aurand 1997). Table 2.6 summarizes the threshold toxicity values used by the US Coast Guard to establish levels of concern associated with a range of environmental exposures to oil and dispersed oil (Aurand et al. 2000). These concentrations and the levels of concern do not directly represent a toxicity value for any one species or habitat. They represent scientific judgment of environmental resource managers of the level of concern that would exist if the exposure concentrations were exceeded in the field.

Table 2.6 Length of Exposure and Level of Concern for Fish and Crustacean/Invertebrates[4]

Length of Exposure	*Level of Concern*	*Sensitive Life Stages*	*Adult Fish*	*Adult Crustacean/ Invertebrates*
0-3 hours	Low	1	10	5
	Med-Low	1-5	10-50	5-10
	Med-High	5-10	50-100	10-50
	High	10	100	50
24 hours	Low	0.5	0.5	0.5
	High	5	10	5
96 hours	High	0.5	0.5	0.5

Table 2.6 is applied as follows. If the threshold for the “low level of concern” is not exceeded for the species of concern, then it is very unlikely that any acute effects among the water column community will be caused by exposure to dispersed oil. For example, for sensitive life history stages an exposure of 1 mg/L for up to 3 hours is listed as a “low” level of concern, while an exposure of 10 mg/L is listed as a “high” concern. This is based on the observation that only a few of the species which have been examined have an LC_{50} value of 1 mg/L or less for a short period, but a greater number have LC50 values near 10 mg/L for tests where concentrations are sustained for 24 to 48 hours. Consequently, the risk to the individuals comprising the community as a whole is low for short-term exposures at 1 mg/L, but increases as values approach 10 mg/L. Because of rapid dilution, chronic effects are unlikely to be a concern, unless there is a mechanism that causes prolonged exposure, such as accumulation in intertidal sediments. These considerations focus on toxic responses among individuals within a species, not the ability of the species to repopulate an area or influence the community as a whole. By applying these types of considerations, field exposure concentrations that would not be expected to cause acute toxicity concerns for aquatic organisms can be established.

[4] Notes: All concentrations are in parts per million (mg/L). Values are intended to indicate threshold levels of concern for resources. For example, if adult fish are exposed to a dispersed oil plume of 100 mg/l for 3 hours, concern should be high. If they are exposed to a 10 mg/L plume for 3 hours, concern should be low because there is little or no potential for acute effects. Toxicity table data is reprinted from Aurand et al. 2000 with permission as a result of this literature search; the results are not from a study of any particular dispersant, dispersant/oil mixture, or species.

The assessment of environmental trade-offs, according to the principles of NEBA (Net Environmental Benefit Analysis)[5], regarding dispersant use should focus on toxicity of dispersed oil in the water column compared to potential impacts that might occur if the oil persists on the water or strands on a shoreline.

2.7 Conclusions

The use of dispersants on large oil spills has not been common. While dispersants have been used on many small oil spills, there is a lack of objective, quantitative documentation about their effectiveness or the ecological consequences of their use.

The exceptions are the *Braer* spill in 1993 and the *Sea Empress* spill in 1996, where dispersants were used in large quantity and which were the subject of extensive follow-up studies of the ecological effects. Both spills occurred in UK waters where the use of dispersants and subsequent at-sea monitoring were planned in advance. The results of ecological studies of the effects of these spills were incorporated into the National Contingency Plan.

In both cases, a large proportion of the spilled oil was dispersed. Severe weather naturally dispersed the oil in the case of the *Braer*, while the judicious application of dispersants abetted dispersal under the less severe weather that prevailed at the *Sea Empress* spill.

Every oil spill is truly unique. The composition of the oil, characteristics of the environment, prevailing weather, and the human environment and resources ensure that no two spills are alike. Consequently, the information and experience gained at one spill response may not be directly transferable to another. However, the *Braer* and *Sea Empress* incidents are the only major spills in which widespread dispersant use was followed by adequate short- and long-term environmental monitoring.

The immediate consequences at both oil spills were similar. Very large quantities of crude oil were dispersed into marine environments with important natural resources and commercial fisheries. In both cases, fisheries were closed for a period and extensive ecological monitoring programs were instigated. Monitoring revealed that the dispersed concentrations sharply increased after the oils were released into sea (and sprayed with dispersant at the *Sea Empress*), but also that these concentrations declined, rapidly to background levels.

The resultant studies came to very many conclusions about the different species and resources that had been affected by the spills and therefore the dispersed oil.. A common theme was that the effects of the dispersed oil were less severe than anticipated. Effects of the dispersed oil were relatively short-lived. There was no discernible effect on plankton populations, which has often been considered to be a probable consequence of high levels dispersed oil in the water column.

[5] NEBA (Net Environmental Benefit Analysis) (Baker J.M., 1995) is the process used to assess the outcome of any oil spill response action by considering it in comparison to the 'base case' of no response. The likely consequences of a proposed response actions, based on available scientific criteria and past experience, are considered so that 'the least worst outcome', based on the reduction of the overall damage that might be caused by an oil spill, without overdue concentration on one particular resource 'segment', is achieved.

In both cases, the ecological effects caused by dispersed oil in the water column were far more transient and much less severe than would have been the case if more spilled oil had come ashore and contaminated sensitive habitats.

Laboratory studies can provide useful information about the performance and toxicity of dispersants; however, their limitations must be fully appreciated. Studies of effectiveness conducted in flasks and small tanks can provide only a relative and crude indicator of dispersant performance under real-world conditions of use. Similarly, the results of standard toxicity tests can help inform decisions about dispersant use, while recognizing that conditions in the field differ radically from those in the laboratory.

Any concerns about the probable effects of elevated dispersed oil concentrations in the marine environment caused by the use of dispersants needs to be balanced with an associated degree of concern for coastal resources that are likely to be impacted if the spilled oil drifts ashore. A consideration of one without the other during an oil spill response operation will produce misleading conclusions. The NEBA (Net Environmental Benefit) (Baker J.M., 1995) process may be used to consider the totality of the effect of response techniques and the overall outcomes.

3.0 Previously Conducted Studies

3.1 Lab Exdet Effectiveness on MC 252 Crude

The following is a preliminary assessment of relative performance of dispersants on the NCP schedule against MC 252 crude oil using the EXDET laboratory effectiveness test method[6].

3.1.1 Objective

The overall objective was to identify the products on the NCP Product Schedule that might be used as an alternative to Corexit products in treating oil from the MC 252 incident using a standard method, the EXDET test.

3.1.2 Approach

The approach was to test all of the dispersants on the NCP product schedule that were effective for dispersing oil discharged in the MC 252 incident. The method used was the EXDET test, a method commonly used in the United States. The dispersants tested were Sea Bratt #4, JD 2000, Dispersit SPC 1000, Biodispers, Nokomis 3-AA, SAF-RON Gold, and Corexit EC9500A.

Corexit is currently used in incident response. The other six dispersants were chosen for testing because they: a) are on the NCP list of dispersants approved by EPA; b) have fewer acute toxicity effects than Corexit, according to information provided by the manufacturer; c) are equally or more effective at dispersing oil, according to information provided by the manufacturer; d) are available or can be produced in the amounts needed to respond to the incident, according to information provided by the manufacturer; and e) samples were available for testing.

3.1.3 Method

A modified version of the EXDET test was run on each of the 7 products. The studies were conducted by Louisiana State University (LSU), Department of Environmental Sciences, Response & Chemical Assessment Team. The test oil was from oil recovered from source. Three replicates were completed for each.

Exactly 250 mL of GOM (Gulf of Mexico) Brine was added to a 250-mL separatory funnel. 1000 uL of the test oil was placed on the water surface and 50 uL of dispersant was added to the surface of the oil from a micropipette, for a dispersant-to-oil ratio of 1:10. The separatory funnel was stoppered and agitated in a wrist-action shaker for 15 minutes after which a small pad of sorbent was added to the funnel to absorb the undispersed oil. The flask was then shaken for an additional 5 minutes. The shaking was then stopped and the water containing dispersed oil was drawn off. The oil in the water and that remaining in the flask were extracted separately using separate volumes of solvent. An index of dispersant effectiveness was calculated based on the amount of dispersed oil in the water versus the total of the amounts in the water and remaining in the flask, all expressed as a percentage.

[6] The Exdet method can be reviewed in Becker et al. 1991, Clark et al 2005, and George-Ares and Clark 2000.

3.1.4 Results and Discussion

Results are summarized in Figure 3.1, below (raw data is provided in Tables 3.1, 3.2, and 3.3). Dispersant performance was reported in terms of the average of three replicates. The numerical value at the top of each bar is the percentage range of test values around the average. The level of dispersion achieved in the control (no dispersant) was 2%, so all dispersant products produced some increased level of dispersion in these tests.

Corexit EC9500A achieved a dispersant effectiveness index of approximately 43%. Effectiveness of Nokomis 3-AA and JD2000 were similar to Corexit EC9500A. Performance of Biodispers was slightly greater than Corexit EC9500A. Performance of Sea Brat #4, Dispersant SPC 1000 and SAF-RON Gold were markedly less than Corexit EC9500A using this method.

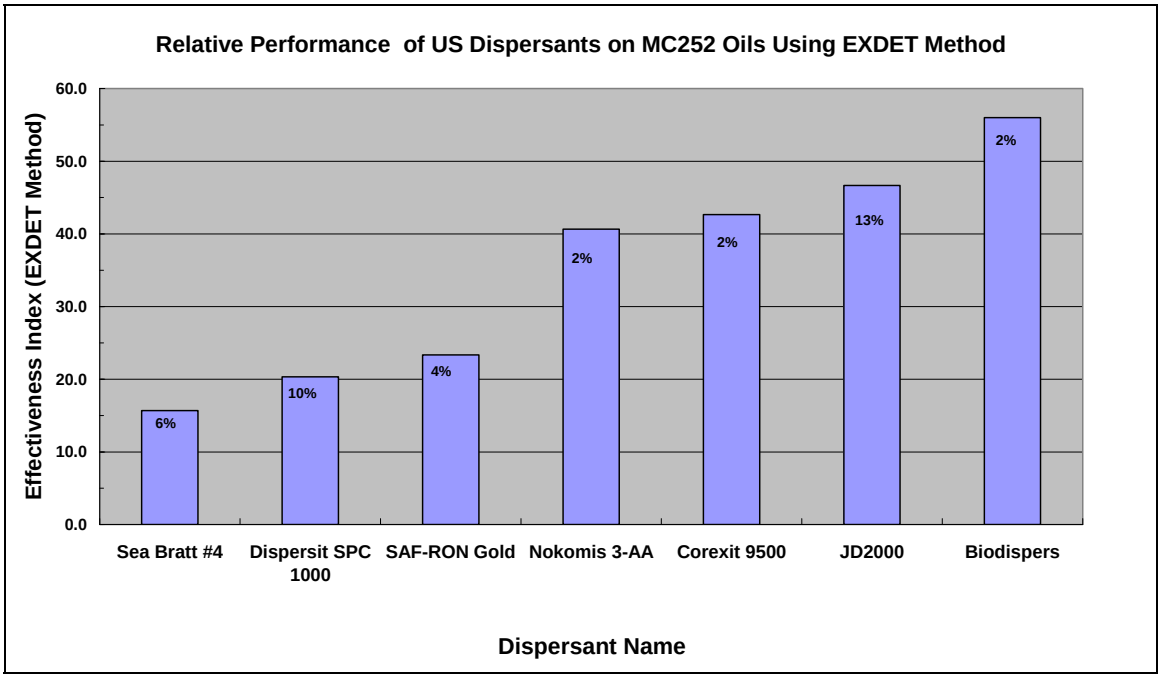

Figure 3.1 Relative Performance of US Dispersants against MC 252 Crude Oil in Exdet Method

The results of this study suggest that the dispersant products Sea Brat# 4, Dispersit SPC 1000 and SAF-RON Gold might perform less well than Corexit EC9500A against fresh MC 252 crude oil. However, it is critically important to recognize several caveats. First, it is not possible to predict dispersant performance at sea quantitatively from the results of any bench scale laboratory test. Rather bench scale tests are useful only to predict relative performance of products. Second, performance of dispersant products may be ranked differently by different dispersant test methods. Workers in the field have learned how to use data from lab tests in planning, in some cases averaging the results of several different methods to produce trends. Finally it is important to recognize that relative dispersant performance against fresh MC252 oils does not necessarily predict relative performance on weathered and emulsified oil.

Table 3.1 Exdet MC 252 Water Phase Test Results

TREATMENT ID	OIL (ml)	DISP. (ml)	INITIAL VOLUME (mL)	FINAL VOLUME (mL)	DILUTION FACTOR	UV/VIS ABSORPTION (460 nm)	MASS OF OIL IN WATER PHASE (mg)
CONTROL #1	1	0.05	250	40	1	0.051	**14**
CONTROL #2	1	0.05	250	40	1	0.050	**14**
CONTROL #3	1	0.05	250	40	1	0.054	**15**
BIODISPERSER #1	1	0.05	250	40	3	0.542	**435**
BIODISPERSER #2	1	0.05	250	40	3	0.591	**475**
BIODISPERSER #3	1	0.05	250	40	3	0.563	**452**
COREXIT 9500 #1	1	0.05	250	40	3	0.396	**319**
COREXIT 9500 #2	1	0.05	250	40	3	0.387	**311**
COREXIT 9500 #3	1	0.05	250	40	3	0.432	**347**
DISPERSIT SPC 1000 #1	1	0.05	250	40	1	0.559	**150**
DISPERSIT SPC 1000 #2	1	0.05	250	40	1	0.513	**137**
DISPERSIT SPC 1000 #3	1	0.05	250	40	1	0.538	**144**
JD-2000 #1	1	0.05	250	40	2	0.563	**302**
JD-2000 #2	1	0.05	250	40	2	0.594	**318**
JD-2000 #3	1	0.05	250	40	2	0.549	**294**
NOKOMIS 3-AA #1	1	0.05	250	40	2	0.493	**264**
NOKOMIS 3-AA #2	1	0.05	250	40	2	0.541	**290**
NOKOMIS 3-AA #3	1	0.05	250	40	2	0.511	**274**
SAF-RON GOLD #1	1	0.05	250	40	1	0.550	**147**
SAF-RON GOLD #2	1	0.05	250	40	1	0.572	**153**
SAF-RON GOLD #3	1	0.05	250	40	1	0.581	**156**
SEA BRAT#4 #1	1	0.05	250	40	1	0.462	**124**
SEA BRAT#4 #2	1	0.05	250	40	1	0.485	**130**
SEA BRAT#4 #3	1	0.05	250	40	1	0.450	**121**

Table 3.2 Exdet MC 252 Non-Water Phase Test Results

TREATMENT ID	OIL (ml)	DISP. (ml)	INITIAL VOLUME (mL)	FINAL VOLUME (mL)	DILUTION FACTOR	UV/VIS ABSORPTION (460 nm)	MASS OF OIL IN NON-WATER PHASE (mg)
CONTROL #1	1	0.05	250	40	4	0.713	**763**
CONTROL #2	1	0.05	250	40	4	0.671	**718**
CONTROL #3	1	0.05	250	40	4	0.689	**738**
BIODISPERSER #1	1	0.05	250	40	3	0.432	**347**
BIODISPERSER #2	1	0.05	250	40	3	0.471	**379**
BIODISPERSER #3	1	0.05	250	40	3	0.449	**361**
COREXIT 9500 #1	1	0.05	250	40	3	0.524	**421**
COREXIT 9500 #2	1	0.05	250	40	3	0.561	**451**
COREXIT 9500 #3	1	0.05	250	40	3	0.550	**442**
DISPERSIT SPC 1000 #1	1	0.05	250	40	4	0.510	**546**
DISPERSIT SPC 1000 #2	1	0.05	250	40	4	0.567	**607**
DISPERSIT SPC 1000 #3	1	0.05	250	40	4	0.521	**558**
JD-2000 #1	1	0.05	250	40	2	0.587	**314**
JD-2000 #2	1	0.05	250	40	2	0.559	**299**
JD-2000 #3	1	0.05	250	40	2	0.598	**320**
NOKOMIS 3-AA #1	1	0.05	250	40	4	0.365	**392**
NOKOMIS 3-AA #2	1	0.05	250	40	4	0.399	**428**
NOKOMIS 3-AA #3	1	0.05	250	40	4	0.348	**373**
SAF-RON GOLD #1	1	0.05	250	40	4	0.495	**530**
SAF-RON GOLD #2	1	0.05	250	40	4	0.458	**491**
SAF-RON GOLD #3	1	0.05	250	40	4	0.467	**501**
SEA BRAT#4 #1	1	0.05	250	40	4	0.636	**681**
SEA BRAT#4 #2	1	0.05	250	40	4	0.592	**634**
SEA BRAT#4 #3	1	0.05	250	40	4	0.651	**697**

Table 3.3 Exdet MC 252 Mass Balance Test Results

TREATMENT ID	OIL (ml)	DISP. (ml)	MASS OF OIL IN WATER PHASE (mg)	MASS OF OIL IN NON-WATER PHASE (mg)	TOTAL OIL MASS (mg)	% OIL DISPERSED
CONTROL #1	1	0.05	14	763	777	2
CONTROL #2	1	0.05	14	718	732	2
CONTROL #3	1	0.05	15	738	752	2
BIODISPERSER #1	1	0.05	435	347	783	56
BIODISPERSER #2	1	0.05	475	379	853	56
BIODISPERSER #3	1	0.05	452	361	813	56
COREXIT 9500 #1	1	0.05	319	421	740	43
COREXIT 9500 #2	1	0.05	311	451	762	41
COREXIT 9500 #3	1	0.05	347	442	789	44
DISPERSIT SPC 1000 #1	1	0.05	150	546	696	22
DISPERSIT SPC 1000 #2	1	0.05	137	607	745	18
DISPERSIT SPC 1000 #3	1	0.05	144	558	702	21
JD-2000 #1	1	0.05	302	314	616	49
JD-2000 #2	1	0.05	318	299	617	52
JD-2000 #3	1	0.05	294	320	614	48
NOKOMIS 3-AA #1	1	0.05	264	392	656	40
NOKOMIS 3-AA #2	1	0.05	290	428	718	40
NOKOMIS 3-AA #3	1	0.05	274	373	647	42
SAF-RON GOLD #1	1	0.05	147	530	678	22
SAF-RON GOLD #2	1	0.05	153	491	644	24
SAF-RON GOLD #3	1	0.05	156	501	656	24
SEA BRAT#4 #1	1	0.05	124	681	805	15
SEA BRAT#4 #2	1	0.05	130	634	764	17
SEA BRAT#4 #3	1	0.05	121	697	818	15

Note: 1 ml of Oil + 50ul Corexit EC9500A Check Standard = 756 mg Total Oil Mass

3.2 Field Studies of Dispersant Effectiveness on MC252 Crude: A Comparison of Three Alternatives to Corexit EC9500A

Conducted May 5-17, 2010, this study tested the performance of three alternative dispersants on fresh MC 252 crude oil in tests at sea at or near the spill site on three dates over the period May 5 to 17, 2010. Dispersants Sea Brat #4, JD2000, and Dispersit SPC 1000 were tested along with Corexit EC9500A.[7] Effectiveness was assessed visually (as per SMART Tier I), and instrumentally using the Turner C3 (C3) instrument to measure in-water oil concentrations under treated slicks (as per SMART Tier II). In addition, the size distribution of oil particles in the water under the treated slicks was measured using a Sequoia LISST-100X instrument, for further confirmation of effectiveness.

The test using Corexit EC9500A produced clear evidence of effective dispersion both visually and instrumentally using the C3. Sea Brat #4 produced visible effectiveness in a test on May 8, but no visible effectiveness in two tests on May 17. The JD2000 product produced visual evidence of effectiveness in May 12 tests, but not in May 17 tests. Dispersit SPC 1000 produced visual evidence of effectiveness in the May 17 test.

Our experience in attempting to test dispersant effectiveness at sea during this spill identified certain challenges. The challenges of actually traversing the spray path with the instruments (where the dispersed oil should be) were evident from some of the vessel track traces. We had been successful in retracing the dispersant spray path in a practice exercise, but operational challenges remained. SMART GPS is extremely useful in repositioning, but there appear to be other challenges. It must be recognized that the level of mixing energy available (wind speeds, presence of breaking waves) varies to a degree among the tests making direct comparison more challenging. In this study we compensated for this by using the vessel bow wave to provide uniform supplemental mixing energy where practicable.

3.2.1 Objective

The purpose of this evaluation was to obtain field data on relative effectiveness of alternative dispersant products that could be compared to laboratory dispersant effectiveness testing. These data are material to the identification of additional dispersants, which might be recommended for use.

3.2.2 Test Protocols

Field test protocols developed by the environmental team specified applying up to 100 gallons of dispersant at a rate of 5 gallons per minute (gpm) from a boat equipped with a spray system (Figures 3.2 and 3.3). To deliver this application, a boom-spray system with downward facing nozzles was installed on the 46' *Grand Bay* (and later, the 46' RW *Armstrong*) fast response vessel (FRV). This was supplemented using a commercial hose and spray nozzle system in order to increase the range of dispersant dose rates possible. This boat can accommodate two totes of product at a time. Transit time from the dock to the spill site ranged from 2 – 4 hours each way. Spotter aircraft are generally required to locate oil patches for treatment.

[7] The Nokomis and Saf-ron Gold products were delivered late in the period and could not be tested due to time limitations.

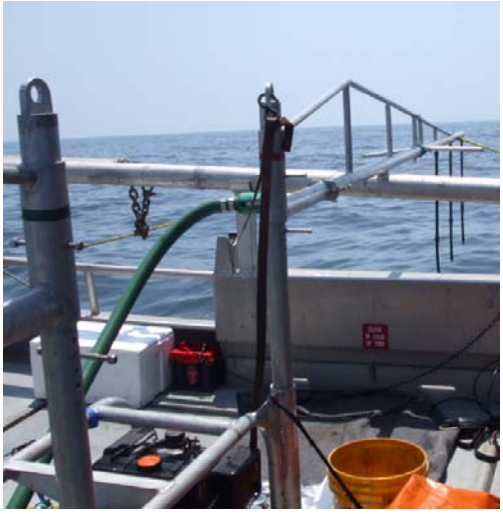

Figure 3.2 The Slickspray 3210

Figure 3.3 46' Fast Response Vessels

It is important that these tests be rapid and easy to implement. The goal is a timely field assessment to meet operational objectives, not a detailed characterization. Therefore, the Tier I and Tier II SMART protocols were used to meet test objectives. Tier I employs the simplest operation, visual monitoring and Tier II combines visual monitoring with in-situ water column monitoring using fluorometry at a single depth (one meter).

Specific protocols include:

- Dispersant coverage rate of 5 gpa or greater;
- Visual observations to assess oil behavior after mixing;
- Fluorometry monitoring upon completion of dispersant application and across the application track;
- Photo documentation when a change is observed.

In order to be of operational value, criteria must be straightforward and rapidly available. Tier I and Tier II observation protocols meet these objectives. Tier I recommends visual observations. Tier II monitoring uses a fluorometer at a 1-meter sampling depth. It shows the relative increase of hydrocarbons over background, which is sufficient for operational evaluation. The specific methodology entails taking a background flourometry reading and transit through the slick prior to spraying dispersant and returning to the starting point and following the same track while spraying dispersant. Upon completion of the spray run, the vessel returned to the starting point again, waited for a minimum of 20 minutes and then ran a sinusoidal path in order to transect the spray path multiple times while collecting fluorometric data.

3.2.3 Evaluation Criteria

Criteria sufficient for the operational interpretation of the visual and fluorometry results include visual observation and fluorometry.

- Visual observation: change in the appearance of the treated slick versus an untreated slick or a visible brown cloud of dispersed oil in the water column might indicate that the dispersant is working
- Fluorometry: any substantial increase in concentration over background indicates dispersion

3.2.4 Results

Between May 5, 2010 and May 17, 2010, tests were conducted using two 46-foot fast response vessels fitted with a Slickspray 3210 spray system. Three NCP-listed dispersants (Sea Brat #4, Dispersit SPC 1000, and JD 2000) were evaluated on fresh oil located near the MC 252 spill source.

3.2.4.1 Alternative Dispersant Test May 8, 2010

On May 8, 2010, at a location about 0.5 miles east of the spill site (28 42140 88 20121) the vessel *Grand Bay* set up to spray Sea Brat #4 dispersant. The oil on the water ranged from sheen to 1 mm or more and appeared to be very fluid.

The SMART team deployed the C3 and ran for about 15 minutes so they could collect background fluorescence data. The boat circled back to the start and ran the same course spraying Sea Brat #4 dispersant. As soon as the dispersant hit the black oil, dispersion was evidenced almost immediately by the presence of a light brown subsurface plume just behind the spray arms (a Tier I verification of positive dispersion, see Figures 3.4 & 3.5, below). The vessel traveled 0.54 miles at about 2 knots to minimize the bow wave pushing oil aside and out of the reach of the spray arms. Total spray time was 14 minutes. After waiting for 15 minutes, the vessel ran transects across the spray path to determine the presence or absence of dispersed oil.

Start 1:16 28 42.140 88 20.121 Stop 1:30 28 42.547 88 20.518

Figure 3.4 Sea Brat #4 Application by Spray Arm

Figure 3.5 Visible Presence of Dispersed Oil Plume

As the vessel followed a sinusoidal track through the spray path, the SMART team monitored for an increased fluorescence reading. As the vessel crossed the spray path, the SMART team reported an

increased reading (a Tier 2 verification for positive dispersion). Each time the vessel passed through the treated path, an increase in reading was observed (see Figures 3.6 and 3.7, below). As the vessel moved beyond the spray track, the value dropped off. This simultaneous reporting of an increase in fluorometer reading at the same time the vessel's GPS track showed a position within the spray track was a strong indicator to that oil was dispersed. The areas highlighted and labeled A, B and C of Figure 3.6 show the enhanced fluorescence readings as the vessel crossed the spray path during the transect run. Based on visual observation and SMART monitoring, Sea Brat #4 did disperse fresh oil.

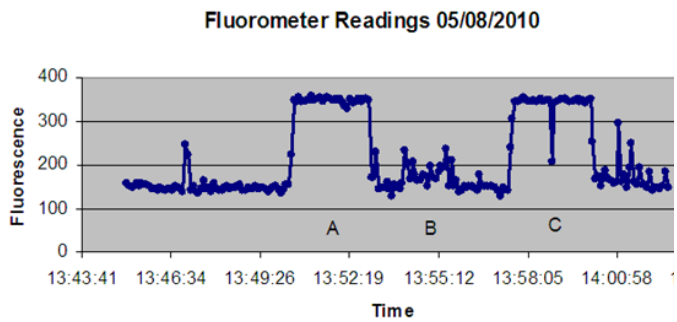

Figure 3.6 Turner C3 Flourometer Readings

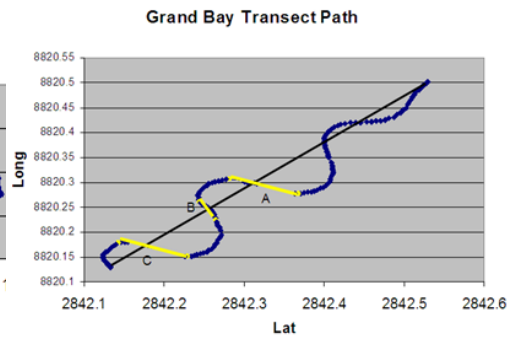

Figure 3.7 Grand Bay Transect Path

3.2.4.2 Alternative Dispersant Tests May 12, 2010

After several days of either not being able to go out due to rough seas or not finding enough oil that could be treated, staff traveled to the spill site with a Turner C3 fluorometer and LISST light scattering particle size detector. For Reference, the source is: 28 44.173 N 88 21.574W and sea state was 3 foot waves and good visibility with sunny weather conditions. Fresh oil was found and the spray arms were deployed.

Upon spraying fresh oil with JD 2000 (Figures 3.8 and 3.9) at 28 44.371 by 88 21.326, the presence of a dispersed oil plume was readily apparent meeting Tier I requirements. Upon spraying the fresh oil with Dispersit SPC1000 (Figures 3.10 and 3.11), the presence of a dispersed oil plume was readily apparent meeting Tier I requirements.

Figure 3.8 JD 2000 Dispersant Applied

Figure 3.9 Dispersed Oil after JD Dispersant Applied

Figure 3.10 Dispersit SPC1000 Applied

Figure 3.11 Dispersed Oil after Dispersit Applied

3.2.4.3 Alternative Dispersant Tests May 17, 2010, Location 1

After several days of not being able to go out due to rough seas, the SL Ross team, aboard the RW Armstrong, traveled to the spill site with a Turner C3 fluorometer and LISST laser particle size detector on board. In order to maximize the utility of the trip, the vessel was loaded with four dispersant samples in either 250 gallon tote tanks or 5 gallon buckets (see picture below): JD 2000, Dispersit SPC 1000, Corexit EC9500A, and Sea Brat #4. A hose with spray nozzle was attached to the spray arm system to allow greater flexibility in dispersant application (see Figures 3.12 and 3.13 below). For reference, the source is: 28 44.173 N 88 21.574W with 3 foot waves, good visibility, and sunny weather conditions. The oil was patchy with small areas of thicker oil surrounded by heavy sheen. Vessel traffic was also problematic.

Figure 3.12 Dispersant Samples

Figure 3.13 Additional Spray Hose

JD2000 was sprayed for 2 minutes at 3 knots using the hand nozzles from the bow to ensure good contact with the oil. This application protocol worked well providing a heavier dose and better controlled application of dispersants than was possible with boom sprayer. This system was used in all of the tests completed on this cruise.

Instrument transects were completed with difficulty due to extensive vessel traffic, e.g., at one point the *Seacor Vanguard* passed directly through the test area and prevented the *Armstrong* from completing its normal transect.

There was no visual evidence of dispersion of the oil in the bow wave energy in this test. There was visible herding of the oil by the dispersant but no visible clouds of dispersed oil. The vessel track, C3 and LISST data are below. Track data show that instrument passes did not intersect the spray track, in part due to need to avoid vessel traffic. The first 500 seconds of SMART C3 data are the oil environment beneath the untreated slick (as per SMART protocol). In the rest, elevated C3 readings may have been due to the instrument breaching at the surface. Upon spraying fresh oil, no dispersed oil plume was observed.

Sea Brat was tested on a patch of thick oil during a 2-minute spray run at 3 knots using the hand nozzles from the bow. No clouds indicative of highly effective dispersion were seen in the bow-wave following the dispersant application. Track data show that instruments transected spray path at several points, despite other vessels. C3 and LISST data show no areas of consistently elevated dispersed oil concentrations. There are several spikes in the C3 traces, but LISST data show that there was no depression of the droplet size, showing that spikes may have been due to instruments breaching rather than due to dispersed oil. Summary: Upon spraying fresh oil, no dispersed oil plume was observed.

Dispersit was applied in the third test, again using the hand nozzles from the bow at 3 knots and for 2 minutes. The oil at this location was thick and fresh. Visible dispersion was seen in the bow wave immediately following application with this dispersant. Peaks in the C3 trace were evident during the run. There were no peaks in the LISST data and no evidence that droplets were smaller in C3 peaks. We were ordered out of the area shortly after we had applied the dispersant so only one truncated instrument pass was possible in this test. Upon spraying fresh oil, the presence of a dispersed oil plume was readily apparent meeting Tier I requirements.

3.2.4.4 Alternative Dispersant Tests May 17, 2010, Location 2

The Armstrong moved to a patch of thick fresh black oil with streaks of red emulsion near the spill site (28 46.285 / 88 28.270) where two more tests were conducted.

Sea Brat was tested again on this thicker oil because the test earlier in the day was completed in a relatively lightly oiled area. As in the previous test with Sea Brat, no significant dispersion was seen in the bow-wave in this test. An instrumental run was done with C3 and LISST. Upon spraying fresh oil, no dispersed oil plume was observed.

The test using Corexit EC9500A was completed for purposes of comparison. This was done on similar oil to the previous Sea Brat #4 test: a two-minute spray from the bow was completed. As in #3 and #4 the dispersant spray was aided with mixing using the vessel wake. Clouds were observed immediately after the passage of the bow wave through the sprayed oil showing that “quick and effective” dispersion of the thick oil patches sprayed. Dispersion was seen in the wake indicating that the dispersant was highly effective. Dispersed oil clouds were also visible in the upper water layer during the short instrument run that was completed. These clouds were scattered so they all may not have been hit with the instruments during the instrument passes. The C3 data are consistent with visual showing numerous consistent peaks. There were peaks in concentration in LISST trace as well, but no consistent reduction

in particle size was associated with concentration peaks. A sample of the oil from this location was taken for potential future analysis. Upon spraying fresh oil, the presence of a dispersed oil plume was readily apparent meeting Tier I requirements.

3.2.4.5 Summary

This study tested the performance of three alternative dispersants on fresh MC 252 crude oil in tests at sea at or near the spill site over the period May 5 to 17, 2010. Dispersants Sea Brat #4, JD2000 and Dispersit SPC 1000 were tested along with Corexit EC9500A. The Nokomis product was delivered late in the period and could not be tested due to time limitations. Effectiveness was assessed visually (as per SMART Tier I), instrumentally using the Turner C3 (C3) instrument to measure in-water oil concentrations under treated slicks (as per SMART Tier II). In addition, the size distribution of oil particles in the water under the treated slicks was measured using a Sequoia LISST-100X instrument, for further confirmation of effectiveness.

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Our experience in attempting to test dispersant effectiveness at sea during this spill identified certain challenges. The challenges of actually traversing the spray path with the instruments (where the dispersed oil should be) were evident from some of the vessel track traces. We had been successful in retracing the dispersant spray path in a practice exercise, but operational challenges remained. SMART GPS is extremely useful in repositioning, but there appear to be other challenges. It must be recognized that the level of mixing energy available (wind speeds, presence of breaking waves) varies to a degree among the tests making direct comparison more challenging. In this study we compensated for this by using the vessel bow wave to provide uniform supplemental mixing energy where practicable.

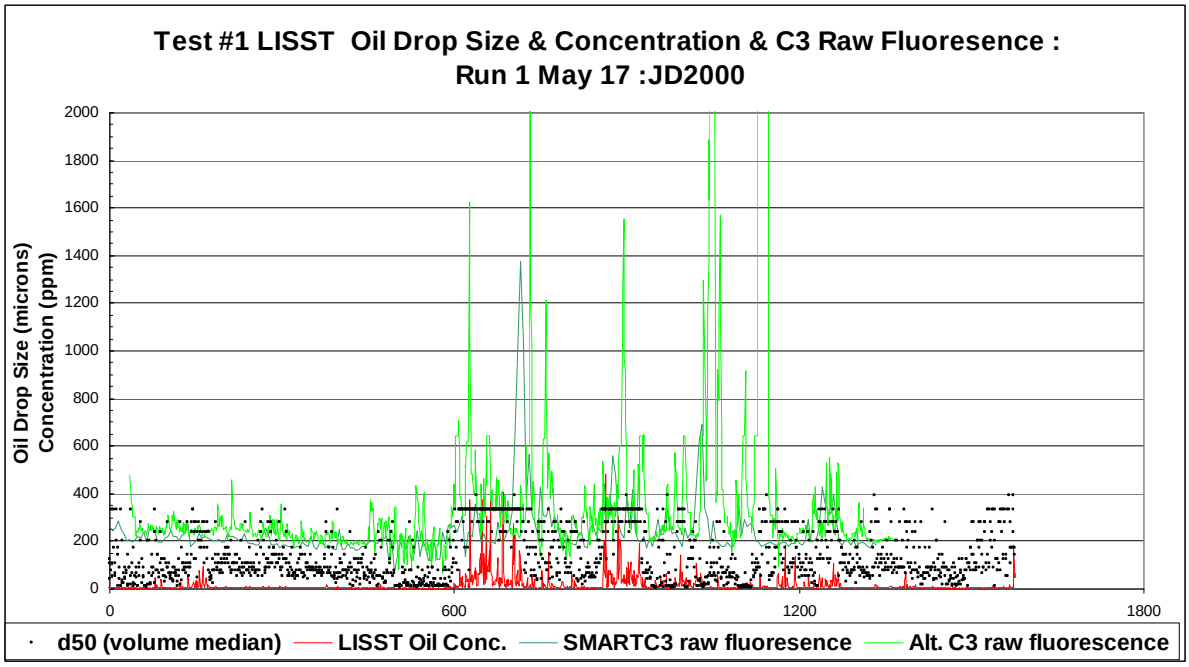

Figure 3.14 LISST Oil Drop Size & Concentration and C3 Raw Fluorescence May 17, 2010 JD 2000 Test

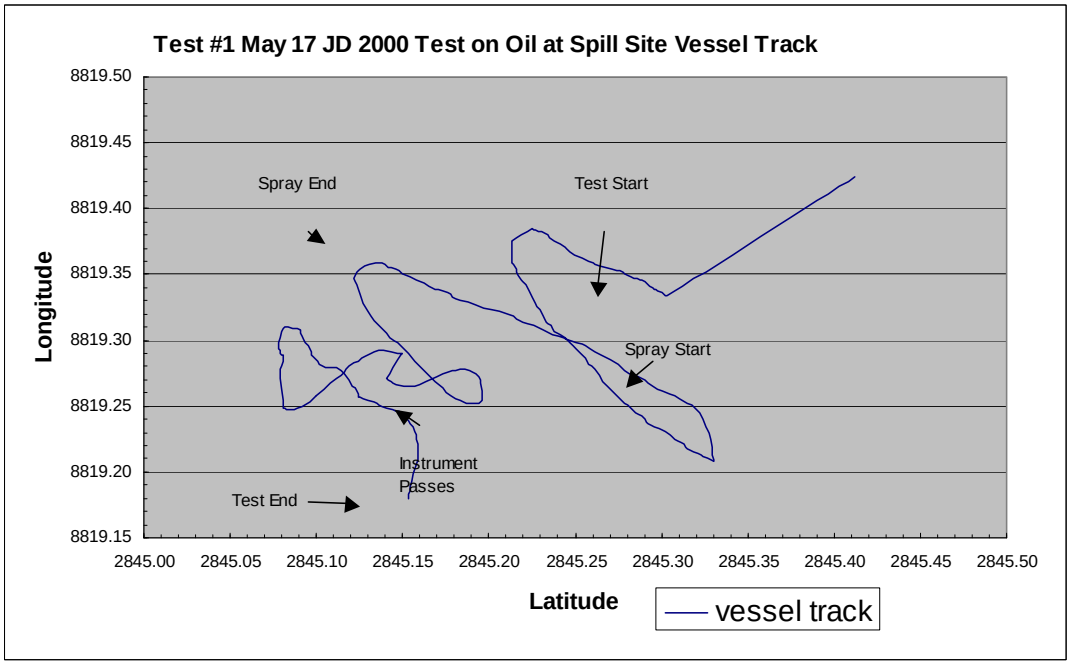

Figure 3.15 Vessel Track for May 17, 2010 JD 2000 Test

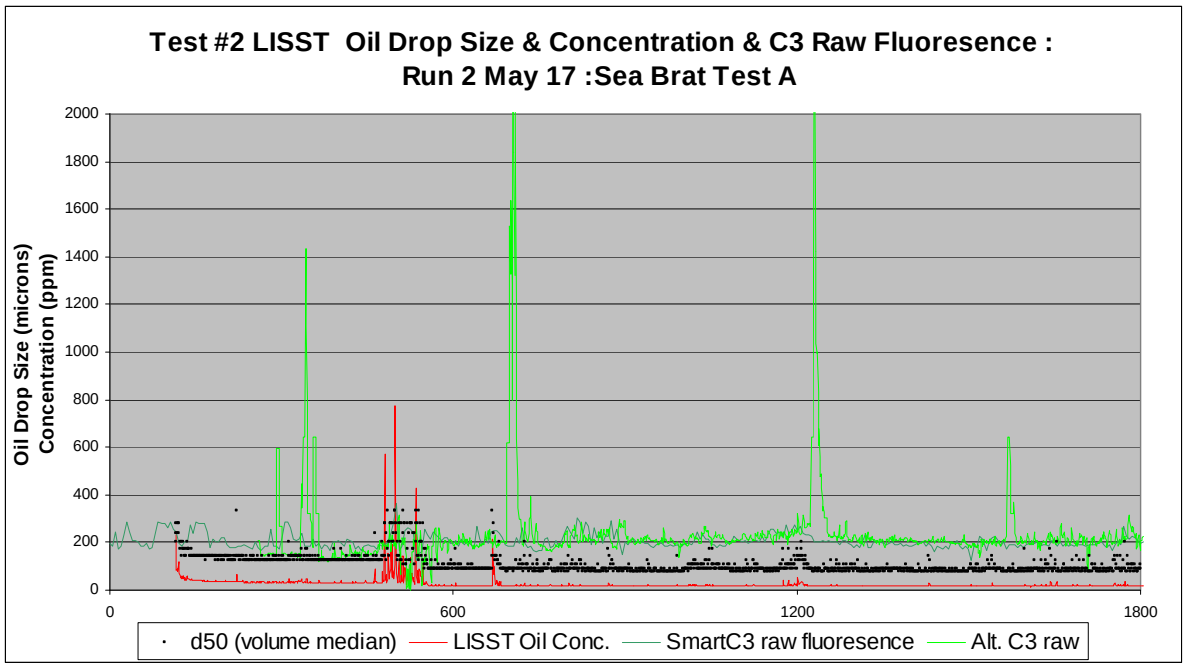

Figure 3.16 LISST Oil Drop Size & Concentration and C3 Raw Fluorescence May 17, 2010 Sea Brat Test A

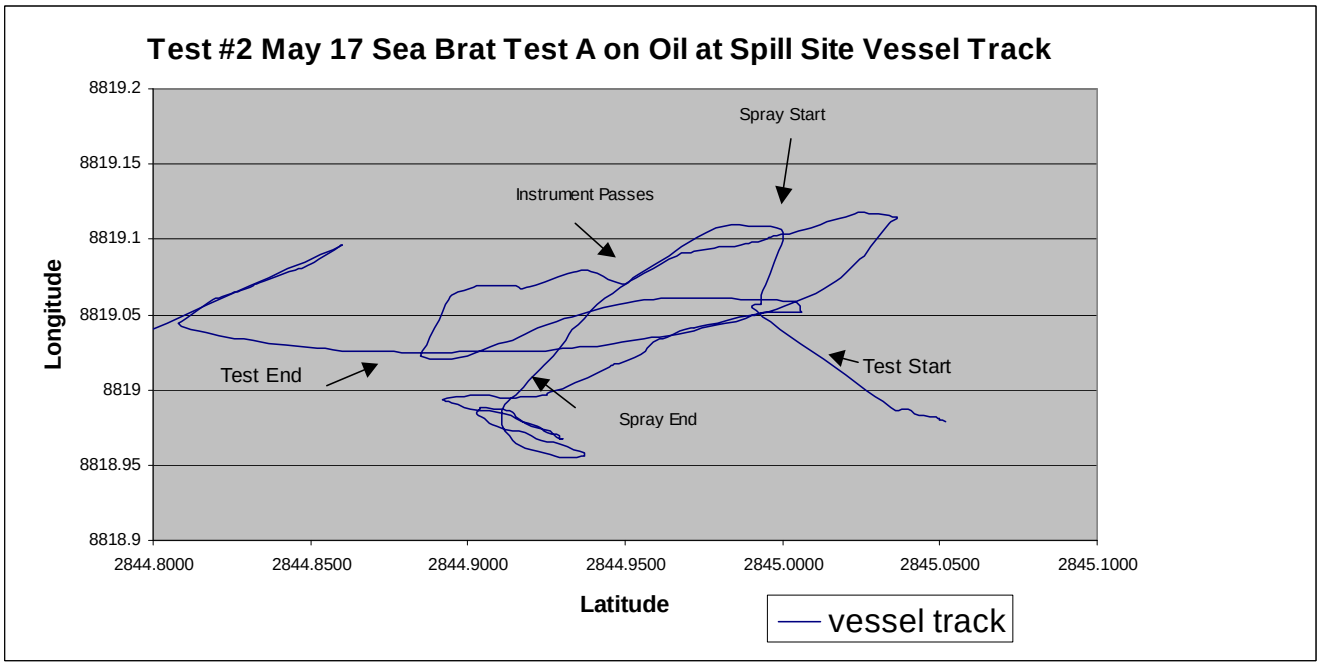

Figure 3.17 Vessel Track for Test #2 May 17, 2010 Sea Brat Test A

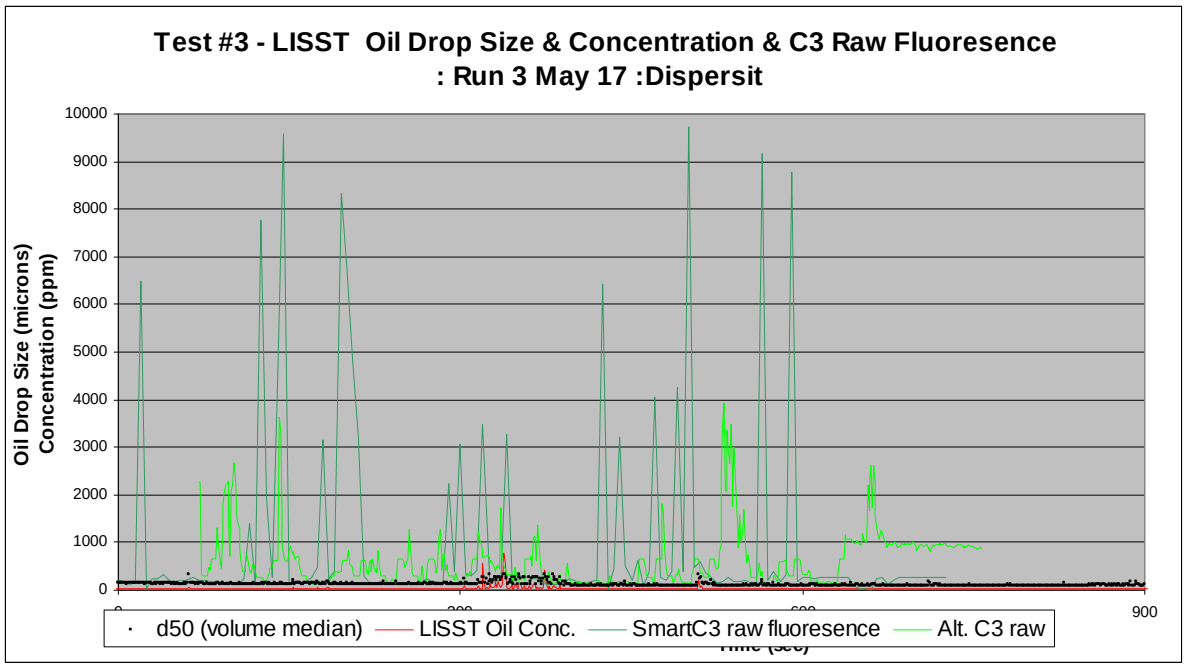

Figure 3.18 LISST Oil Drop Size & Concentration and C3 Raw Fluorescence May 17, 2010 Dispersit Test

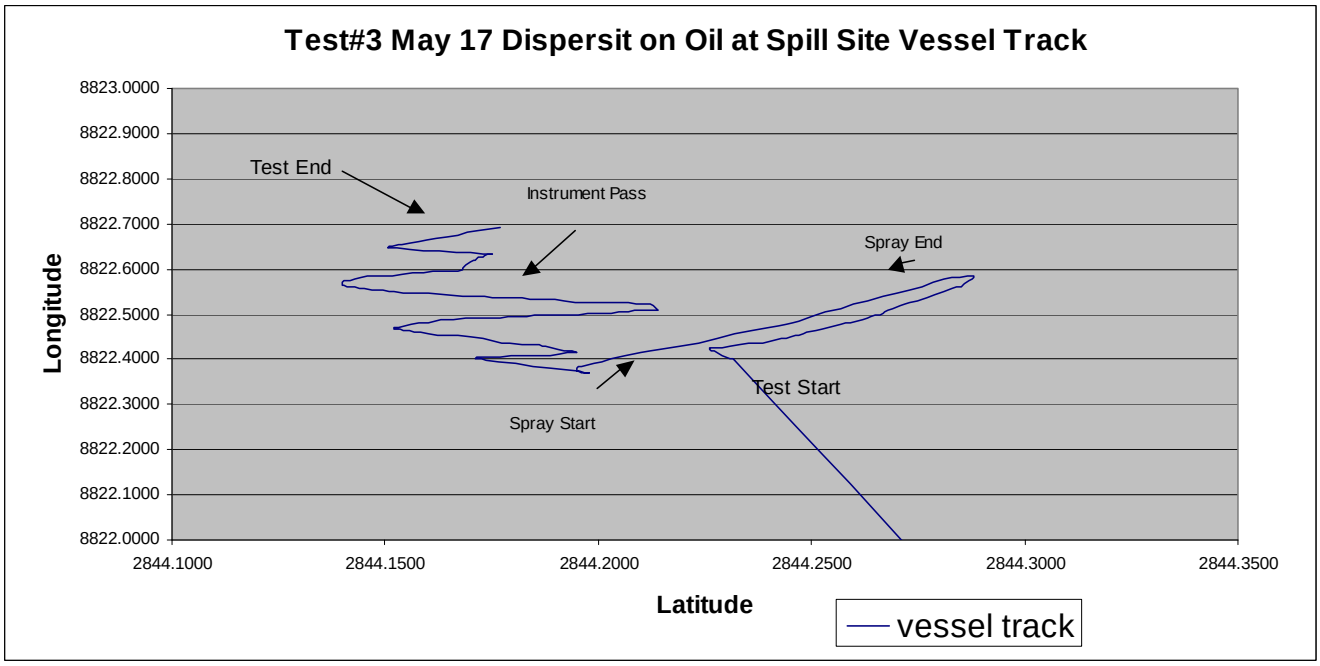

Figure 3.19 Vessel Track for Test #3 May 17, 2010 Dispersit Test

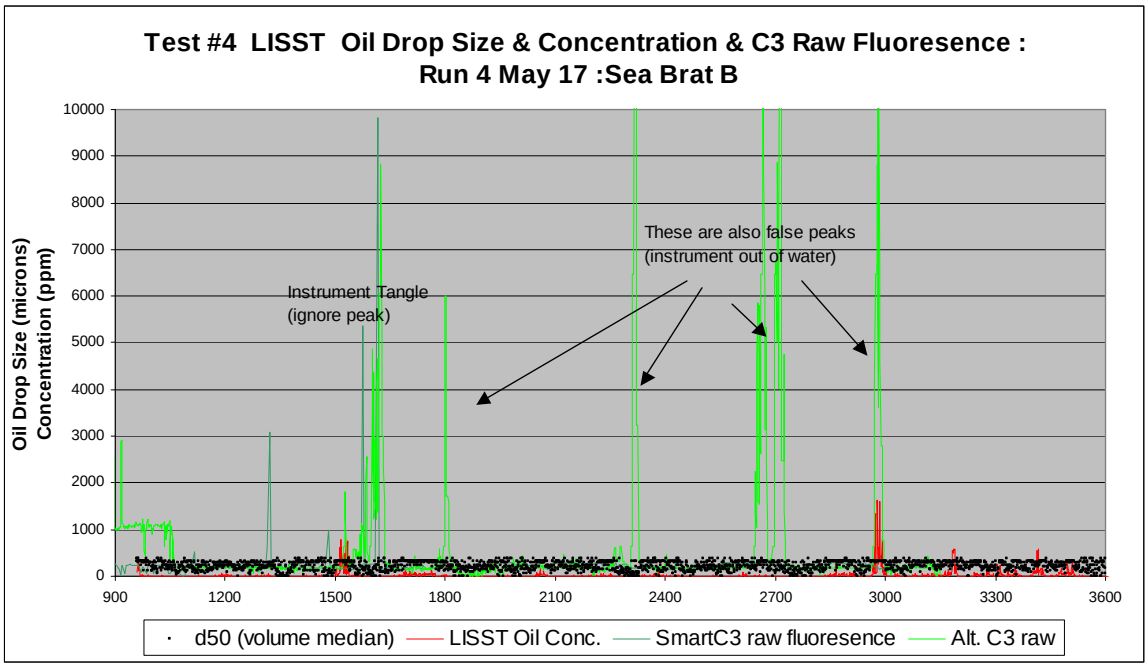

Figure 3.20 LISST Oil Drop Size & Concentration and C3 Raw FluorescenceMay 17, 2010 Sea Brat B

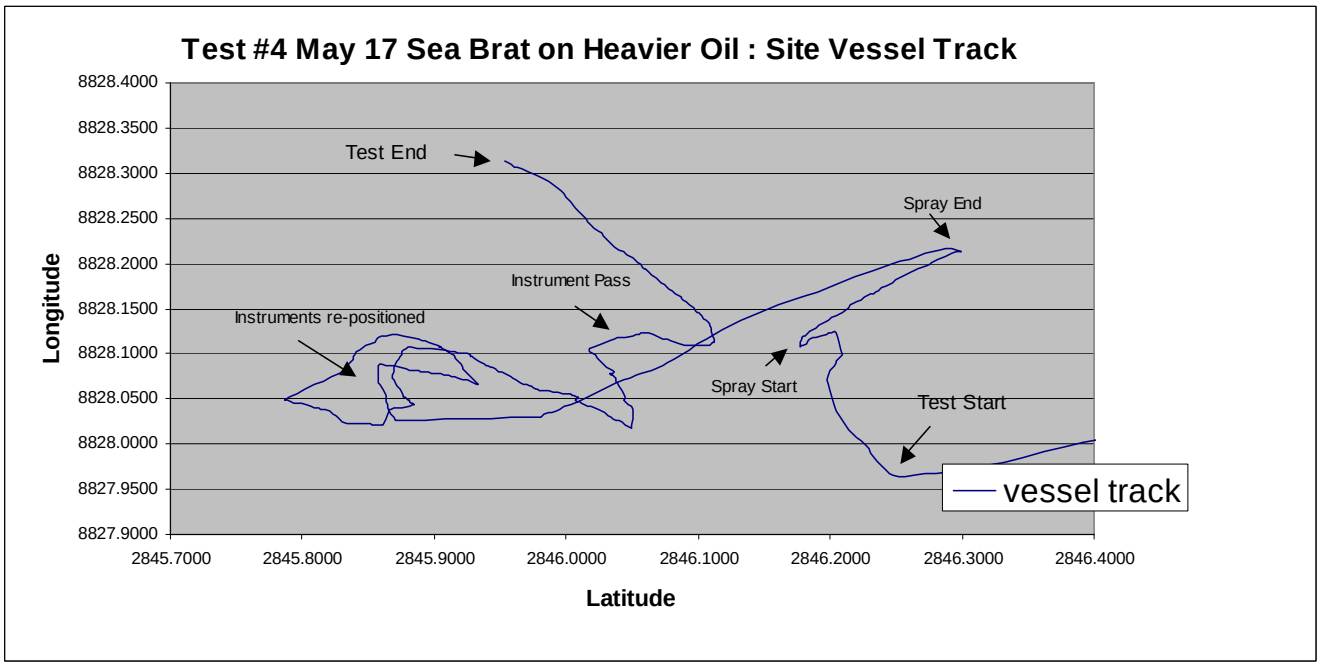

Figure 3.21 Vessel Track for Test #4 May 17, 2010 Sea Brat on Heavier Oil

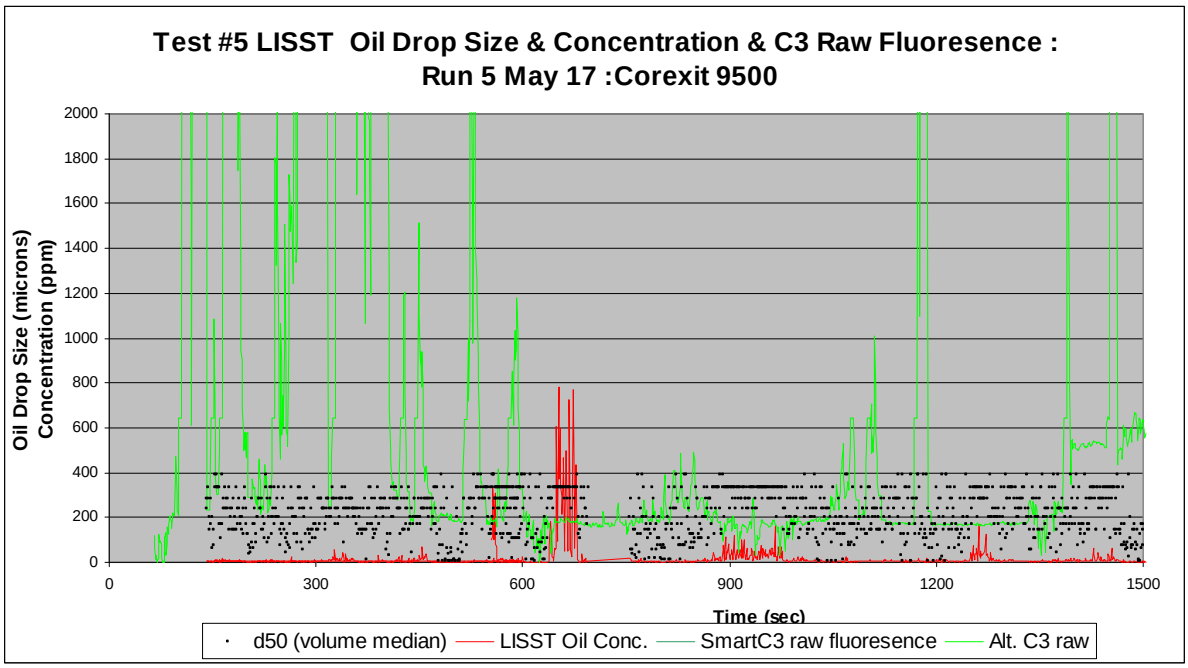

Figure 3.22 LISST Oil Drop Size & Concentration and C3 Raw Fluorescence May 17, 2010 Corexit EC9500A

3.3 Review of Toxicity Concerns Based on Formulae of Candidate Dispersants

3.3.1 Overview

The BP scientific team conducted an evaluation to addresses issues of persistence in the environment, ecotoxicity, and mammalian toxicity for the dispersants evaluated in this study. The products evaluated included:

- Sea Brat #4;
- Nokomis 3-AA;
- Nokomis 3-F4;
- Dispersit SPC 1000;
- Corexit EC9500A;
- Corexit EC9527A; and
- Saf-Ron Gold

The initial evaluation focused on information provided on the products' Material Safety Data Sheet (MSDS; see Appendix C). It quickly became apparent that these did not provide sufficient information for a thorough evaluation. Manufacturers were contacted to provide detailed composition information. Some manufacturers provided complete descriptions of component names, CAS#s and percent composition (Corexit EC9500A, Corexit EC9527A, Dispersit). Other manufacturers provided names of components but not a complete list of CAS#s or the percent composition. So the specific identity of components was not always clear (Sea Brat #4, Saf-Ron Gold). One manufacturer has not yet agreed to a nondisclosure agreement and the analysis was based on the MSDS description of composition (Nokomis).

Hazard classifications that were available with BP Product Safety databases were evaluated first. These include hazard classifications used under the EU or Canadian classification and labeling rules as well as GHS classifications that have been received from product suppliers, published on regulatory agency lists, or derived by BP Product Stewardship staff. In addition, data on aquatic toxicity as well as mammalian toxicity summaries were also evaluated. Sources included the U.S.EPA IRIS and HPV Programs, OECD SIDS Assessment Reports, component MSDSs, and other summary documents.

In addition, lists of priority hazardous substances were checked to see if any of the components would be considered an environmental hazard based on evaluations conducted by government agencies involved with preservation of water quality. The lists that were surveyed included those developed under OSPAR and the EU Water Framework Directive, and the Canadian Environmental Protection Act. In addition an examination of whether the U.S. EPA had developed Water Quality Criteria for the components (or known breakdown products of those components) was carried out.

Product component identity along with available hazard and toxicity information was inserted into a spreadsheet to facilitate comparisons. This spreadsheet is provided in Appendix D, which contains confidential business information on the product formulas[8].

[8] Appendix D in its entirety can be obtained by written request to BP. It is not included in the body of the document to protect sensitive business confidential information.

A literature review was conducted to identify the potential toxicity of each chemical that is known to be present in the seven dispersants that were tested. In order to complete this report in the time frame requested by the agencies, our review did not include an evaluation of the exposure or dose of the chemical required to exhibit such effects, and it did not compare those exposure or dose levels to the levels found in each dispersant. Such comparisons are needed to draw conclusions about the likely toxicity of any dispersant product in the field.

3.3.2 Mammalian Toxicity Review

3.3.2.1 Sea Brat #4

Components were generally of low mammalian toxicity. One component is a solvent that is in common usage. There have been findings of red blood cell hemolysis and other effects in animals. However toxicity studies have shown that, due to differences in metabolism, several of the effects observed in animal studies would not be expected in humans at routine occupational exposure levels. An occupational exposure guideline (TLV) has been developed for this component by the American Conference of Governmental and Industrial Hygienists and it is expected that these would be followed by application workers. Lower level residual concentrations in dispersed oil would not be expected to be of concern. This component has undergone a review through the U.S. EPA IRIS program. Reference values (oral and inhalation) have been derived based on effects observed in animal studies and modified by known human/animal differences in compound metabolism and kinetics.

Concerns for other components were primarily as possible eye and respiratory irritants, but appropriate workplace protection should prevent these effects for application workers. Residues of dispersant in treated oil would not be expected to cause dermal irritation if clean-up workers follow precautions to prevent dermal contact with the weathered oil.

The product contained a component that could have nonylphenol (NP) as a degradation product. The parent compound is of low acute mammalian toxicity. The NP degradation product is a concern primarily from an environmental perspective, although concerns have been expressed regarding the potential human health hazards of NP as well due to endocrine disruption activity observed in some laboratory studies. Concerns about this class of components are discussed further in the ecotoxicity review.

3.3.2.2 Nokomis 3-F4

Detailed composition data have not yet been provided so review is based on MSDS component listing of nonylphenol polyethylene ethoxylate (<5%). This substance could have NP as a degradation product. The parent compound is of low acute mammalian toxicity. The NP degradation product is a concern primarily from an environmental perspective, although concerns have been expressed regarding the potential human health hazards of NP as well due to endocrine disruption activity observed in some laboratory studies. Concerns about this class of components are discussed further in the ecotoxicity review.

3.3.2.3 Nokomis 3-AA

Detailed composition data have not yet been provided so review is based on MSDS component listing of alkylphenol ethoxylate (<10%). A review of the CAS# provided indicated the component could also be referred to as polyethylene glycol nonylphenyl ether. This substance could have nonylphenol as a

degradation product. The parent compound is of low acute mammalian toxicity. The NP degradation product is a concern primarily from an environmental perspective, although concerns have been expressed regarding the potential human health hazards of NP as well due to endocrine disruption activity observed in some laboratory studies. Concerns about this class of components are discussed further in the ecotoxicity review.

3.3.2.4 Dispersit SPC 1000®

Like other dispersants that were reviewed, several components present an eye, skin and respiratory irritation hazard especially if material is applied as an aerosol of undiluted material. However, proper personal protective equipment should protect application workers. Low level residues of dispersant in treated oil would not be expected to cause dermal irritation if clean-up workers follow precautions to prevent dermal contact with the weathered oil. Otherwise components appear to be of low toxicity.

One component of the product has been found to produce tumors in mice in long term bioassay, but the finding was not repeated in rats. Studies of mechanism indicate little relevance of the finding for humans. These data have been reviewed by both International Agency for Research on Cancer (IARC) and the National Toxicology program (as part of the Report on Carcinogens) but neither group has listed it as a carcinogen.

3.3.2.5 Corexit ® EC9500A

Like other dispersants that were reviewed, several components present an eye, skin and respiratory irritation hazard especially if material is applied as an aerosol of undiluted material. However, proper personal protective equipment should protect application workers. Low level residues of dispersant in treated oil would not be expected to cause dermal irritation if clean-up workers follow precautions to prevent dermal contact with the weathered oil. Otherwise components appear to be of low toxicity.

One component has been evaluated under U.S. EPA HPV Program and a Screening-Level Hazard Characterization has been prepared. The material has been well studied and no data gaps were identified for the category. The acute oral and dermal toxicity was low. It did not show carcinogenic potential in rats. Decreased weight gain was observed in a three generation study in rats but no reproductive or developmental effects were observed. No Observed Adverse Effects Levels (NOAELs) have been derived based on the data. The component is approved for use in over-the-counter drugs as well as cosmetics.

3.3.2.6 Corexit EC9527AA

Like other dispersants that were reviewed, several components present an eye, skin and respiratory irritation hazard especially if material is applied as an aerosol of undiluted material. However, proper personal protective equipment should protect application workers. Low level residues of dispersant in treated oil would not be expected to cause dermal irritation if clean-up workers follow precautions to prevent dermal contact with the weathered oil. Otherwise components appear to be of low toxicity.

One component is a solvent that is in common usage. There have been findings of red blood cell hemolysis and other effects in animals. However toxicity studies have shown that, due to differences in metabolism, several of the effects observed in animal studies would not be expected in humans at routine occupational exposure levels. An occupational exposure guidelines (TLV) has been developed for this component by the American Conference of Governmental and Industrial Hygienists and it is

expected that these would be followed by application workers. Lower level residual concentrations in dispersed oil would not be expected to be of concern. This component has undergone a review through the U.S. EPA IRIS program. Reference values (oral and inhalation) have been derived based on effects observed in animal studies and modified by known human/animal differences in compound metabolism and kinetics.

One component has been evaluated under U.S. EPA HPV Program and a Screening-Level Hazard Characterization has been prepared. The material has been well studied and no data gaps were identified for the category. The acute oral and dermal toxicity was low. It did not show carcinogenic potential in rats. Decreased weight gain was observed in a three generation study in rats but no reproductive or developmental effects were observed. No Observed Adverse Effects Levels (NOAELs) have been derived based on the data. The component is approved for use in over-the-counter drugs as well as cosmetics.

3.3.2.7 Saf-Ron Gold ®

A CAS# was only provided for one component. This component could have a degradation product that has been identified as a concern from an ecotoxicity standpoint regarding possible endocrine disruption effects. The parent compound is of low acute mammalian toxicity. The degradation product is a concern primarily from an environmental perspective, although concerns have been expressed regarding the potential human health hazards as well due to endocrine disruption activity observed in some laboratory studies. Concerns about this class of components are discussed further in the ecotoxicity review.

Though not identified specifically, the other components do not appear to be of concern from a mammalian toxicity standpoint. As with other products there would like be an irritation hazard for application workers and proper personal protective equipment should be worn.

3.3.3 Ecotoxicity Review

3.3.3.1 Sea Brat #4

The majority of the product's constituents are of low environmental concern because they are either biodegradable well or are of low aquatic toxicity. One component in the formulation is a concern because it may degrade to nonylphenol (NP). The component and NP are listed on the OSPAR List of Chemicals for Priority Action (Update 2007) under the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic. They are also listed as a restricted or prohibited substance in the EU (Annex XVII of the REACH regulation). NP is identified as a "Priority Hazardous Substance" under the EU Water Framework Directive (Directive 2008 /105 / EC). Because of these listings, the use of this component is restricted in applications that may result in environmental exposure in several regions outside of the U.S. NP has also been evaluated by U.S. EPA and an Aquatic Life Ambient Water Quality Criteria has been derived.

Based on the available scientific information, NP and parent compounds of NP may be persistent in the environment, especially under anaerobic conditions. NP can have both immediate (acute) or long-term harmful effects on aquatic organisms and may affect biological diversity. Both NP and NPEs have been reported to cause a number of estrogenic responses in a variety of aquatic organisms. NPs bind to the estrogen receptor, resulting in the expression of several responses both in vitro and in vivo, including

vitellogenin induction in fish. Chronic toxicity values (No-Observed-Effect Concentrations, or NOECs) for NP are as low as 6 µg/L in fish and 3.9 µg/L in invertebrates (Canada).

Background documents relevant to this category of components, NP and related substances are presented in Appendix B.

3.3.3.2 Nokomis 3-F4

Detailed composition data have not yet been provided so review is based on MSDS component listing of nonylphenol polyethylene ethoxylate (NPE). A review of the scientific literature reveals that NPEs can be quickly degraded through a mechanism of stepwise loss of the ethoxy groups to form lower ethoxylated congeners, carboxylated products and NP. The component and NP are listed on the OSPAR List of Chemicals for Priority Action (Update 2007) under the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic. They are also listed as a restricted or prohibited substance in the EU (Annex XVII of the REACH regulation). NP is identified as a "Priority Hazardous Substance" under the EU Water Framework Directive (Directive 2008 /105 / EC). Because of these listings, the use of this component is restricted in applications that may result in environmental exposure in several regions outside of the U.S. NP has also been evaluated by U.S. EPA and an Aquatic Life Ambient Water Quality Criteria has been derived.

Based on the available scientific information, NP and parent compounds of NP may be persistent in the environment, especially under anaerobic conditions. NP can have both immediate (acute) or long-term harmful effects on aquatic organisms and may affect biological diversity. Both NP and NPEs have been reported to cause a number of estrogenic responses in a variety of aquatic organisms. NPs bind to the estrogen receptor, resulting in the expression of several responses both in vitro and in vivo, including vitellogenin induction in fish. Chronic toxicity values (No-Observed-Effect Concentrations, or NOECs) for NP are as low as 6 µg/L in fish and 3.9 µg/L in invertebrates (Canada).

Background documents relevant to this category of components, NP and related substances are presented in Appendix B.

3.3.3.3 Nokomis 3-AA

Detailed composition data have not yet been provided so review is based on MSDS component listing of alkylphenol ethoxylate (<10%) in the hazardous ingredients listing. A review of the CAS# indicated the component could be referred to as polyethylene glycol nonylphenyl ether. This component is a concern because it may degrade to nonylphenol (NP). The component and NP are listed on the OSPAR List of Chemicals for Priority Action (Update 2007) under the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic. They are also listed as a restricted or prohibited substance in the EU (Annex XVII of the REACH regulation). NP is identified as a "Priority Hazardous Substance" under the EU Water Framework Directive (Directive 2008 /105 / EC). Because of these listings, the use of this component is restricted in applications that may result in environmental exposure in several regions outside of the U.S. NP has also been evaluated by U.S. EPA and an Aquatic Life Ambient Water Quality Criteria has been derived.

Based on the available scientific information, NP and parent compounds of NP may be persistent in the environment, especially under anaerobic conditions. NP can have both immediate (acute) or long-term harmful effects on aquatic organisms and may affect biological diversity. Both NP and NPEs have been

reported to cause a number of estrogenic responses in a variety of aquatic organisms. NPs bind to the estrogen receptor, resulting in the expression of several responses both in vitro and in vivo, including vitellogenin induction in fish. Chronic toxicity values (No-Observed-Effect Concentrations, or NOECs) for NP are as low as 6 µg/L in fish and 3.9 µg/L in invertebrates (Canada).

Background documents relevant to this category of components, NP and related substances are presented in Appendix B.

3.3.3.4 Dispersit SPC 1000®

The scientific literature suggests that several components of Dispersit SPC 1000 formulation are considered to rapidly biodegrade once released into the aquatic environment. However, it is important to note that it is not always clear – like with other dispersants that were reviewed in this short timeframe – if biodegradability in the marine environment or under anoxic conditions (e.g. in sediments) will also be satisfactory. Those components which do not rapidly biodegrade are with high probability not acutely harmful to aquatic organisms or no toxic effects occur at the range of solubility.

3.3.3.5 Corexit ® EC9500A

The scientific literature suggests that several components of Corexit EC9500A formulation are considered to rapidly biodegrade once released into the aquatic environment. However, it is important to note that it is not always clear – like with other dispersants that were reviewed in this short timeframe – if biodegradability in the marine environment or under anoxic conditions (e.g. in sediments) will also be satisfactory. Those components which do not rapidly biodegrade are with high probability not acutely harmful to aquatic organisms or no toxic effects occur at the range of solubility.

3.3.3.6 Corexit EC9527A

The scientific literature suggests that several components of Corexit EC9527A formulation are considered to rapidly biodegrade once released into the aquatic environment. However, it is important to note that it is not always clear – like with other dispersants that were reviewed in this short timeframe – if biodegradability in the marine environment or under anoxic conditions (e.g. in sediments) will also be satisfactory. Those components which do not rapidly biodegrade are with high probability not acutely harmful to aquatic organisms or no toxic effects occur at the range of solubility.

3.3.3.7 Saf-Ron Gold ®

The supplier for this dispersant formulation provided only one CAS# of the Saf-Ron Gold formulation. This component can degrade to a compound that has been identified as an environmental pollutant. This degradation product is considered to considered to be toxic as defined in Section 64 of the Canadian Environmental Protection Act, 1999 (CEPA 1999), is listed on the OSPAR List of Chemicals for Priority Action (Update 2007) under the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, and is also identified as a “Priority Hazardous Substance” under the EU Water Framework Directive (Directive 2008 /105 / EC). The disclosed compound and degradation products have similar toxicological properties as NP and NPE and because they can be are present in similar environmental compartments, relevant data on these compounds have been reviewed in

supporting documentation for environmental adverse effects in Appendix D[9]. Based on some assessments, estrogenicity of the degradation product in some organisms may be greater than that of NP.

3.3.4 Summary of Mammalian and Ecotoxicity

The review of components in these products indicates that overall there would not be significant concerns from a mammalian toxicity standpoint. Several would be expected to produce irritation at high dose levels, but the effects can be avoided in dispersant application workers through proper controls and proper personal protective equipment. A literature review indicates that a few of the components have been found to produce specific effects in laboratory studies in animals. However in each case there has been a more detailed review of the observed effects. A closer review of mechanism of action and the dose levels that produced those effects (Appendix D)[10] provides assurance that these would not be a concern for dispersant use as it is presently being conducted.

The majority of the constituents of the 7 reviewed dispersants products are of relatively low environmental concern because they are either considered to biodegrade well and/or are of low aquatic toxicity.

The key issue that has arisen in the ecotoxicity review is that 4 out of the 7 dispersants; Sea Brat #4, Nokomis 3-AA, Nokomis 3-F4, and Saf-ron Gold contain or degrade to a component that has been identified as an endocrine disruptor which may persist in the environment. Some of the products contain small amounts of this material, and one product may contain up to 10% of this component. Because a large volume of dispersants may required to respond to this incident over a period of weeks to months, it is important to consider whether prolonged use, in large volumes, would have effects that are not normally considered in EPA's evaluation of dispersant chemicals. These chemicals are legally restricted or prohibited in some jurisdictions (e.g. Canada or the EU) especially for those industrial applications which potentially result in release to the aquatic environment. Based on the available scientific information, these compounds can biodegrade rapidly to nonylphenol (NP) or related compounds once they enter aquatic environments. They are then considered persistent, especially under anaerobic conditions and can have an immediate (acute) or long-term toxic effect (including endocrine disrupting activity) or potentially affect biological diversity. These compounds are primarily a concern from an environmental standpoint, although concerns have been expressed regarding the potential human health hazards of NP as well due to endocrine disruption activity observed in some laboratory studies. The components of concern and/or their degradation products are listed on the OSPAR List of Chemicals for Priority Action (Update 2007) under the OSPAR Convention for the Protection of the Marine Environment of the North-East Atlantic, and identified as a "Priority Hazardous Substance" under the EU Water Framework Directive (Directive 2008 /105 / EC). Most are listed as a restricted or prohibited substance in the EU (Annex XVII of the REACH regulation). NP has also been evaluated by U.S. EPA and Canada Environment and in the U.S., Aquatic Life Ambient Water Quality Criteria have been derived (see Appendix B).

Considering the volume of dispersant that is required to treat the MC 252 incident, the products that do not contain the components that degrade to NP or related compounds are the preferred products for

[9] Appendix D in its entirety can be obtained by written request to BP. It is not included in the body of the document to protect sensitive business confidential information.
[10] See previous footnote.

use at this site, in the conditions observed here. Of the NCP listed products that were reviewed, the Corexit products (EC9500A and EC9527A) and the Dispersit SPC 1000 products did not contain these components of concern.

4.0 Summary and Recommendations for Current Study

4.1 Summary of Available Information

This section, presents an overview of the relevant information from the literature review (Section 2), the results of the efficacy testing and formulation evaluations (Section 3) and proposes a path forward to resolve remaining uncertainties related to both toxicity and efficacy under more realistic conditions. It begins with a series of summary statements explaining BP's position on the critical issues related to any decision to change dispersants.

With respect to available toxicity testing information:

- EPA requirements for toxicity testing for listing on the NCP Product Schedule were designed as screening criteria. They do not attempt to recreate the conditions or exposures that would be found in the marine environment during an actual spill event.
- The measured toxicity for Corexit EC9500A and EC9527A in the NCP Product Schedule are within the average range of toxicities of the other products listed on the NCP Product Schedule, given the variability of laboratory toxicity tests.
- There is more laboratory and field data available for the Corexit® products than for any other dispersant (see bibliography). These data reflect a wide range of test organisms, exposure durations and conditions, including spiked exposure testing, which is more reflective of the actual situation during field application.
- All of the available toxicity information for Corexit® EC9500A and EC9527A indicates that they do not represent a toxicity concern at the concentrations and dilutions anticipated for surface or subsurface application. As summarized in Section 2, the toxicity associated with dispersant alone is much less significant than that of the oil component of dispersed oil.

With respect to available information on product formulations:

- Sea Brat #4, Nokomis 3-AA, Nokomis 3-F4, and Saf-ron Gold contain a class of compounds known to act as endocrine disruptors, which may bioaccumulate in marine organisms, biodegrade slowly, and potentially persist in the marine environment for years.
- The Corexit products do not contain this class of compounds and, based on manufacturer's information, reach their maximum biodegradation rate within days to several weeks.
- Toxicity protocols used to evaluate compounds for listing on the NCP Product Schedule are not intended for evaluating chronic impacts, such as those caused by endocrine disruptors.

With respect to available information on laboratory and field efficacy testing:

- Laboratory efficacy tests do not necessarily reflect results which could be expected in field applications.
- The EPA protocol for listing on the NCP Product Schedule uses a swirling baffled flask test which, while higher energy than previous designs, is still lower energy than tests used elsewhere in the world.
- The results of the EPA testing protocol were designed as a screening protocol, and are not intended to rank field effectiveness, nor should they be used to try and indicate probable dispersant effectiveness in the field.

- The Corexit® products were shown to be effective in the EPA protocols, and are highly effective in higher energy laboratory testing protocols used elsewhere.
- Of products available in sufficient volume, in the Exdet tests (Section 3), the Corexit® products were the highest in effectiveness; Sea Brat #4 was the lowest.
- Unlike Sea Brat #4, the Corexit® products have a history of effective use in the Gulf of Mexico at actual, but relatively small, spills, where they were judged to be highly effective.
- In actual field tests, only Corexit EC9500A performed consistently.

4.2 Recommendations Given Consideration of the Current Situation

All parties in this evaluation have the same objective: the minimization of impacts to the marine environment. Dispersant use, whether surface or subsurface, has the benefit of minimizing impacts to sensitive shoreline, and allowing dilution of oil droplets, which are then subject to biodegradation within the water column. This process, while having environmental consequences, is much less of a risk than shoreline impacts (see Section 2). That said, it is important to ensure that the products in use represent the best overall choice, based on availability, effectiveness, and toxicological concerns.

While efficacy and toxicity are certainly issues to consider, the larger concern is the potential consequence of switching to a product containing a class of compounds of biological and regulatory concern in both the United States and throughout the world. **All of the dispersant products on the NCP that are 1) available in sufficient volumes and 2) meet the EPA's Addendum 2 toxicity requirements contain products that degrade to NP.**

Of all products on the EPA's NCP Product Schedule that were available in sufficient volumes, only Dispersit was both *less toxic* (albeit slightly) than the Corexit products and *did not contain chemicals that degrade to NP*. And while Dispersit SPC1000 appears to be very slightly less toxic according to the NCP product schedule, it was also less effective with respect to the MC 252 Exdet test and performed inconsistently in the field test.[11]

By comparison, the tests using Corexit EC9500A produced clear evidence of effective dispersion of MC 252 in the field both visually and instrumentally; it also performed better in the Exdet test. Even though it does not meet EPA's Addendum 2 toxicity requirements, **based on the currently available data, Corexit EC9500A remains the most logical choice**. The data supporting these conclusions is summarized in Table 4.1.

Nevertheless, BP remains committed to obtaining additional relevant information on toxicity in order to conform with the directives laid out in Addendum 2 (Appendix A) and confirm the currently available data. The dispersant products selected for additional testing included: Corexit EC9500A, Dispersit SPC1000, Nokomis 3-AA, Nokimis 3-F4, Saf-Ron Gold, and Sea Brat #4. These products are both 1) less toxic than Corexit[12], and 2) available in sufficient quantities. JD 2000 and ZI400 were not selected because their toxicity values for LC50 tests on Mendia or Mysidosis species were worse than Corexit EC9500A's values.

Section 4.3 contains protocols for additional toxicity testing, currently underway. While these evaluations will not address our concern about endocrine distruptors, they will provide additional

[11] Furthermore, it does not meet the toxicity level requirements laid out in Addendum 2.
[12] As measured by LC50 for Medidia and Mysidosis.

information on the relative toxicity of the dispersants in question, when present in the environment as "dispersed oil droplets." Furthermore, section 4.4 contains protocols for additional efficacy testing, currently underway. These tests will utilize more realistic testing conditions in terms of simulation of actual environmental conditions.

Table 4.1 Summary Table

NCP List	*Availability*			*Toxicity*		*Effective-ness %*	*Contain NP*	*Further Tests*
	Days to 1st Prod	*Days to 150K gal stock*	*Max Daily Prod*	*LC50 Menidia*	*LC50 Mysidosis*			
Biodispers	NR		10000*	-	-	-	-	-
Corexit EC9500A	0	3	48000	2.61	3.40	54.70	No	Yes
Corexit EC9527A	0	3	48000	4.49	6.60	65.40	No	No***
Dispersit SPC 1000	9	14	70000	7.90	8.20	100.00	No	Yes
Finasol OSR 52	No Response from Manufacturer			-	-	-	-	-
JD 109	No Longer Manufactured			-	-	-	-	-
JD 2000	6	10	50000	3.59	2.19	77.80	No	No**
Mare Clean 200	No Longer Manufactured			-	-	-	-	-
Neos AB3000	No Response from Manufacturer			-	-	-	-	-
Nokomis 3-AA	7	12	70000	34.22	20.16	65.70	Yes	Yes
Nokomis 3-F4	7	12	70000	100.00	58.40	64.90	Yes	Yes
Saf-Ron Gold	-	-	150000	9.25	3.04	53.80	Yes	Yes
Sea Brat #4	6	11	150000	23.00	18.00	60.70	Yes	Yes
ZI 400	15	-	25000	8.35	1.77	89.8	Yes	No**

NR – not relevant; max daily production insufficient
* Concentrate diluted 1:10 per manufacturer's instructions
** More toxic than Corexit EC9500A
***Corexit EC9500A and EC9527A are essentially the same formulation with a different solvent. Nalco notified BP that they had problems sourcing this solvent. Between sourcing problems and little incentive to change (similar toxicity and effectiveness results), it was determined that testing this dispersant was not useful.

4.3 Proposed Toxicity Study Protocol

This "Rapid Toxicity Evaluation" is designed to examine this last factor acute species impacts from the dispersed oil. Since this evaluation needs to be completed within approximately one week from initiation, the design will utilize a limited number of species and short exposure periods. Since hydrocarbon analysis must be performed, the toxicity tests will be completed in five days, allowing two days for detailed hydrocarbon analysis and result compilation. It is understood that a robust laboratory toxicity testing program should be conducted to consider additional species, chronic exposures including endocrine disruptor testing, and population impacts. However, the current time constraints will only permit this rapid evaluation.

It is well documented that laboratory preparations of dispersed oil are not equivalent to field exposures, since they do not account for dilution. As a result, laboratory toxicity data should not be used to predict actual toxicity in real world conditions. Additionally, traditional LC50 tests require solutions to be made at significantly higher concentrations than those found at actual spills where dispersants have been used. As a result, this laboratory testing will compare relative dispersant(s) behaviors with this source oil, using a single loading rate of oil equivalent to 0.1 mm surface oil slick.

The results of this Rapid Toxicity Evaluation, when considered in conjunction with the other factors listed above, will aid in making dispersant selection decisions.

4.3.1 Testing Objective

This testing is proposed as a "Rapid Toxicity Evaluation" of available dispersants for use on the BP MC 252 spill. The dispersants have been selected for testing based on the following three criteria:

- Currently listed on the EPA NCP product schedule;
- Commercially available in sufficient quantities to treat this ongoing spill; and
- Are less toxic based on LC50 tests of Menidia and Mysidosis than the incumbent product, Corexit EC9500A.

The objective of this testing is to determine the relative acute toxicity of each dispersant when applied to the source oil. This testing will involve the application of each dispersant to a fixed volume of oil at a standard dispersant to oil ratio (DOR). Weathered oil will be used to approximate surface application conditions with dispersant added at a 1:20 DOR. Fresh oil will be used to approximate subsea application conditions with dispersant added at a 1:50 DOR. The reduced DOR for subsea application is based on recent modeling results indicating less dispersant is required because of the high encounter rate when the dispersant is added directly to oil flowing from the riser head.

4.3.2 Methodology

4.3.2.1 Test Species

Three different species have been selected for testing (Figure 4.1):

- Americamysis bahia (previously Mysidopsis bahia) 7-14 day juveniles;
- Artemia salina (brine shrimp) newly hatched; and

- Brachionus plicatilis (marine rotifer) newly hatched.

The first two species are commonly used in EPA waste water effluent testing. Additionally, this mysid is currently being used in field toxicity testing of dispersed oil samples collected in conjunction with aerial dispersant application. The third species is included as a quick screen field test currently being used on the two research vessels supporting the deepsea dispersed oil plume characterization. It is included here for comparison with shipboard testing on dispersed oil samples collected during ongoing subsea dispersant operations.

Figure 4.1 a) Americamysis bahia b) Artemia salina c) Brachionus plicatilis

4.3.2.2 Exposure Regime

For this rapid evaluation, a continuous 24-hour exposure (static, non-renewal) will be conducted. There are two discretely different scenarios for dispersant application at this spill, aerial and subsea.

Aerial dispersant application is targeting weathered oil outside of the dispersant exclusion zone around the source of the spill. This oil is present in a variety of weathered states from approximately 1 day to greater than 30 days. To approximate surface application conditions, oil will be weathered in the lab, then dispersed at a 1:20 DOR using the solution preparation method described below.

Subsea dispersant application is targeting fresh oil released at the riser head. Fresh, untreated oil has been collected from the source. This fresh oil will be used to approximate subsea application conditions with dispersant added at a 1:50 DOR using the solution preparation method described below. The reduced DOR for subsea application is based on recent modeling results indicating less dispersant is required because of the high encounter rate when the dispersant is added directly to oil flowing from the riser head.

4.3.2.3 Solution Preparation

This rapid toxicity assessment will examine chemically enhanced water accommodated fraction (CE-WAF[13]) solutions made from both fresh and weathered oil. To ensure standardization between tests, oil will be weathered in the lab. Fresh will be measured gravimetrically and weathered by 20% through evaporation in a fume hood at room temperature for approximately 8 hours (Figure 4.2). Weathered crude oil is distinguished from fresh or unweathered crude oil by the loss of the low molecular weight constituents such as the normal hydrocarbons less than n-C12, the alkylbenzenes and, to some extent, naphthalene and its alkyl homologues (NOAA 1997[14]).

Due to animal handling considerations, a maximum of six dispersants can be tested simultaneously (Appendix E). The six that have been initially selected are:

- Corexit® EC9500A
- Sea Brat #4
- Nokomis 3-F4
- Nokomis 3-AA
- Saffron Gold
- Dispersit SPC 1000™

In addition, animals will be exposed to an oil only solution (both fresh and weathered) known as a Water Accommodated Fraction (WAF)[15]. All exposure solutions will be prepared according to Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF) protocols[16]. An introduction to the CROSERF work is provided as reference material in Appendix E.

The oil and dispersant will be measured by mass using Hamilton gas-tight syringes and dispensed into glass aspirator bottles containing 2 L of 35 ppt seawater with approximately 20% headspace (Figure 4.3). WAF solutions will be prepared by low energy (no vortex) mixing of water and oil (both fresh oil and weathered oil WAFs will be prepared). CE-WAF solutions will be prepared by 20-25% vortex mixing of water and oil (both fresh and weathered oil will be prepared). Both WAF and CE-WAF solutions will be covered with aluminum foil and stirred for 18 hours, the CE-WAF rested for three hours prior to experimental use. Sample preparation will be tracked using the data sheet provided in Appendix E.

A reference cadmium toxicant test will be conducted with each test species to provide a measure of relative sensitivity for the test organisms.

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[13] Chemically Enhanced Water Accommodated Fraction (CE-WAF): A lab prepared solution derived from addition of a chemical dispersant to oil floating on seawater, resulting in a relatively stable population of bulk material droplets (1-70 micron diameter).

[14] National Oceanic and Atmospheric Administration (NOAA). 1997. Integrating Physical and Biological Studies of Recovery from the Exxon Valdez Oil Spill. NOAA Technical Memorandum NOS ORCA 114. 238 p.

[15] Water Accommodated Fraction (WAF): A lab prepared solution derived from low energy (no vortex) mixing of test material (an oil or petroleum product) which is essentially free of particulates of bulk material (>1 micron diameter).

[16] Coelho, G. 2004. Summary of Laboratory Methods Developed by the Chemical Response to Oil Spills: Ecological Effects Research Forum (CROSERF). Ecosystem Management & Associates, Inc. EM&A Report 04-01. Lusby, Maryland. 27 p.

4.3.2.4 Animal Handling

Mysids and brine shrimp will be purchased from MBL Aquaculture (Sarasota, FL) and Aquatic Research Organisms (Hampton, NH). The mysids will be acclimated to 35 ppt by the aquaculture facilities in advanced, then shipped overnight and held in the laboratory for 2-days to allow the animals to recover from transport. 1-L open beakers will be used as the exposure chamber for the mysids. The brine shrimp and rotifers will be hatched in the laboratory. 250-mL open beakers will be used as the exposure chamber for the brine shrimp, and the Rototox kit test wells will be used for the rotifer exposure chamber. Seawater salinity, dissolved oxygen, pH and temperature will be monitored during each experiment in a subset of the containers as well as throughout animal culturing. Fluorescent tube artificial lighting will be used to provide a photoperiod of 16 hours light and 8 hours dark.

No vertebrate species will be used during this rapid toxicity evaluation.

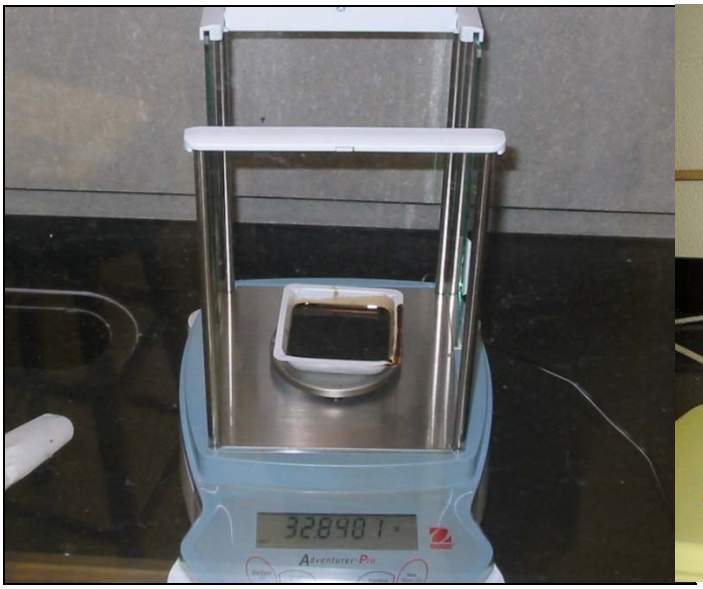

Figure 4.2 Weathering the Oil Gravimetrically in the Laboratory

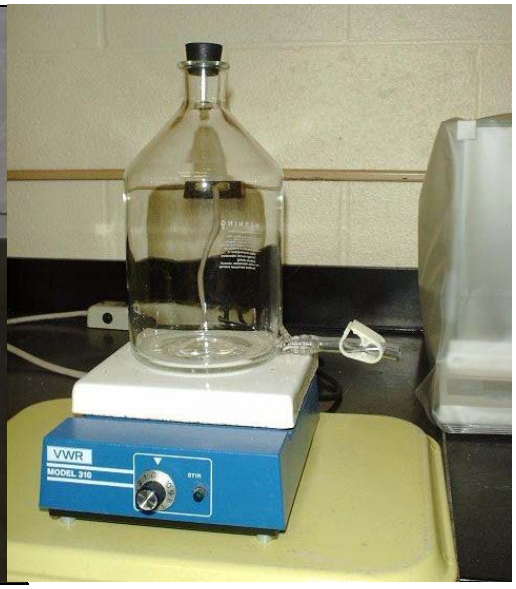

Figure 4.3 Aspirator Bottle and Magnetic Stirrer

This set up is essential when performing the oil and dispersed oil tests. This is a 2L-aspirator bottle with a short piece of clamped-off hosing on the aspirator port and a magnetic Teflon stir bar in the bottle. Seven of these set ups will be utilized. Five CE-WAF preparations (using five different dispersants with the source oil), a WAF preparation (source oil only), and an untreated seawater control.

4.3.2.5 Chemical Analysis

The Modified EPA Method 8270 will be used since the list of PAHs is expanded to include the alkylated homologs, using GC/MS in the selected ion monitoring (SIM) mode. Detection levels should be 1 ppb for individual PAHs. Samples from the WAF and CE-WAF solutions will be collected in 1-liter amber bottles immediately after the solutions are prepared (T=0). A second set of sample water will be collected at the conclusion of each exposure (T=24 hrs). These samples will be packed in Styrofoam coolers and overnight shipped with ice packs to the Louisiana State University hydrocarbon testing laboratory. This laboratory, run by Dr. Ed Overton, is conducting the hydrocarbon analysis for field collected samples. Use of this lab will ensure consistent analytical methodology between this lab study and the field work.

Reference cadmium toxicant solutions will be analyzed using an inductively coupled plasma mass spectrometer.

4.3.2.6 Waste Handling

All waste generated during these toxicity tests will be properly handled in accordance with MSDS and Good Laboratory Practices. All waste will be disposed in accordance with local, state, and Federal rules and regulations.

4.3.3 Testing Timeline

Day 1

- Prepare the WAF and CE-WAF of fresh oil for use in Test 1 (24-hr prep)
- Begin weathering the fresh oil for Test 2

Day 2

- Initiate Test 1: Mysid 24-hour static exposure, fresh oil WAF and CE-WAF
- Test 1 WAF and CE-WAF samples sent for HC analysis
- Prepare the WAF and CE-WAF of weathered oil for use in Test 2

Day 3

- Initiate Test 2: Mysid 24-hour static exposure, weathered oil WAF and CE-WAF
- Test 2 WAF and CE-WAF samples sent for HC analysis
- Terminate and count Test 1
- Prepare the WAF and CE-WAF of fresh oil for use in Test 3
- Begin weathering the fresh oil for Test 4

Day 4

- Initiate Test 3: rotifer and Artemia 24-hour static exposure, fresh oil WAF and CE-WAF
- Test 3 WAF and CE-WAF samples sent for HC analysis
- Terminate and count Test 2
- Prepare the WAF and CE-WAF of weathered oil for use in Test 4

Day 5

- Initiate Test 4: rotifer and Artemia 24-hour static exposure, weathered oil WAF and CE-WAF
- Test 4 WAF and CE-WAF samples sent for HC analysis
- Terminate and count Test 3

Day 6

- Terminate and count Test 4
- Tabulate raw mortality data for all four tests

Day 7

- Receive hydrocarbon chemistry results
- Compile results and submit data

4.4 Proposed Efficacy Study Protocol

4.4.1 Test Tank[17]

1.2 m x1.2 m x 10m tank with a wave paddle at one end, beach at the other.

The tank is filled to 85 cm depth with salt water at the required test salinity and temperature.

Waves with 15 cm amplitude and 1.5 second period used in tests.

Oil is contained in the center of the tank and kept from the side-walls using a 0.75m x 1m rectangular, submerged, air bubble containment system.

4.4.2 Dispersant Application

Either by full-scale overhead spray nozzles or by syringe.

Dispersant dose rate dependent on test objective.

4.4.3 Test Procedure

1. Weigh approximately 750 ml of the test oil and place the oil in the containment zone.
2. Start waves at 39 cpm (this generates a consistent mixing energy).
3. Apply dispersant at the desired DOR.
4. Continue mixing for 30 minutes.
5. Stop the wave paddle and recover the remaining surface oil by skimming into a wide-mouthed sep-funnel.
6. Heat the collected oil in a warm-water bath to break any emulsion that may have formed during the test.
7. Decant the water from the collection funnel and weigh its contents.
8. Compare the weight of the collected oil to that initially placed on the surface to determine the dispersant effectiveness.

4.4.4 Proposed for the MC 252 Oil and Alternative Dispersant Testing

1. Complete an initial series of tests with the MC 252 oil to determine the minimum Corexit EC9500A dispersant dosage necessary to achieve full dispersion in the tank test. This will provide a benchmark for comparison of the other dispersants. The maximum dosage that will be

[17] Detailed descriptions of the equipment and methods used can be found in papers authored by Belore in 2000 and 2002 Arctic and Marine Oil Spill Conference Proceedings.

considered in this test series will be a 1:20 Dispersant-to-Oil Ratio (DOR). If Corexit EC9500A does not completely disperse the MC 252 at this dosage then a 1:20 DOR will be used in the initial screening tests. All dispersants initially will be tested using the benchmark DOR.

2. If the measured effectiveness of an alternative dispersant is less than that of Corexit EC9500A at the benchmark DOR the test will be repeated two more times to provide replicate data for the dispersant.

3. If an alternative dispersant achieves full dispersion at the benchmark DOR the dispersant dosage will be reduced to determine the lowest dosage required to achieve complete dispersion to establish a measure of its improved efficacy over Corexit EC9500A. Three tests at the reduced dosage will be completed to provide replicate data.

4. All tests will be completed using identical water temperatures and salinities matching those present at the MC 252 spill site.

5. All tests will be completed using identical mixing energies and dispersant application methods. Dispersant will be applied to the oil on the water surface by syringe to provide more precise control over the dispersant dosing (as opposed to using an over-head spray system).

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Hundreds of scientific papers have been written concerning all aspects of oil spill dispersants. These have been published in proceedings of conferences, notably:

- The International Oil Spill Conferences held in North America every 2 years from 1969 until 2005 and then in 2008. A searchable database is available: http://www.iosc.org/papers/search. This has over 2,800 papers, abstracts, and proceedings in the archive. Papers accepted for publication by IOSC for conferences in 1995, 1997, 1999, 2001, 2003 and 2005 are included. Abstracts since 1969 are included as are the full texts of proceedings since IOSC 1995.
- The Arctic and Marine Oilspill Program (AMOP) Technical Seminars held in Canada annually from 1977 until the present.
- The Interspill conferences held in Europe every 3 years since 2000
- The SPILLCON conferences held in Australia in 2000, 2002, 2004 and 2007.

Papers on dispersants have been published in many journals including:

- Marine Pollution Bulletin
- Environmental Science & Technology
- Environmental Toxicology & Chemistry
- Ecotoxicology & Environmental Safety
- Journal of Environmental Engineering
- Spill Science and Technology Bulletin (published from 1998 until 2002)

The Louisiana Universities Marine Consortium (LUMCON) has established a searchable database of references specifically on oil spill dispersants. This database is on line at http://www.lumcon.edu//library/dispersants and consists of nearly 2,000 citations found in the journals and conference proceedings listed above, plus government reports and 'grey' literature on research related to oil spill dispersants from 1960 to June 2008.

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APPENDICES

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Appendix A: EPA Dispersant Monitoring and Assessment Directives, and Related Documents

1. Summary of EPA's Dispersant Monitoring and Assessment Directive for Subsurface Dispersant Application.
2. Dispersant Monitoring and Assessment Directive for Subsurface Dispersant Application. May 10, 2010.
3. Dispersant Monitoring and Assessment Directive for Subsurface Dispersant Application – Addendum 1. May 14, 2010.
4. Dispersant Monitoring and Assessment Directive [for Subsurface Dispersant Application] – Addendum 2. May 20, 2010.
5. Letter to Rear Admiral Mary Landry, US Coast Guard, and Samuel Coleman, US Environmental Protection Agency Region 6 in response to Addendum 2. May 20, 2010.
6. Dispersant Monitoring an Assessment Directive[for Subsurface Dispersant Application] – Addendum 3. May 26, 2010.

Appendix B: Regulatory Documents Concerning Nonylphenol and its Ethoxylates

1. Bi-national Framework for Identifying Substances of Potential Threat to the Great Lakes Basin. Test Case: Nonylphenol and its Ethoxylates (NPEs). (November 2008).
2. Canadian Environmental Protection Act, 1999; Priority Substances List Assessment Report; Nonylphenol and its Ethoxylates. April 2001.
3. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on Environmental Quality Standards in the Field of Water Policy and et cetera. Official Journal of the European Union 24.12.2008 L 348.84.
4. European Union's Priority Substances and Certain Other Pollutants (According to Annex II of the Directive 2008/105/EC).
5. OSPAR Commission, OSPAR Convention for the Protection of the Marine Environment Hazardous Substances Series: Nonylphenol/Nonylphenolethoxylates 2001 (2004 Update).
6. OSPAR Commission, OSPAR Convention for the Protection of the Marine Environment List of Chemicals for Priority Action (2007 Update) Reference Number 2004-12.
7. Restrictions on the Manufacture, Placing on the Market, and Use of Certain Dangerous Substances, Preparations and Articles. Official Journal of the European Union 29.5.2007 L 136/129.
8. UK Environment Agency. Nonylphenol Ethoxylate. March 2010.
9. US Environmental Protection Agency Office of Water. Aquatic Life Ambient Water Quality Criteria – Nonylphenol. EPA-822-R-05-005 December 2005.
10. US Environmental Protection Agency Design for the Environment Fact Sheet.

Appendix C: MSDS for Dispersants

1. Corexit EC9500A MSDS
2. Corexit EC9527A MSDS
3. Corexit EC9580A MSDS
4. Dispersit MSDS
5. Nokomis 3-F4 and Nokomis 3-AA MSDS
6. Sea Brat #4 MSDS
7. Saf-ron Gold MSDS

Appendix D: Business Confidential Information about Dispersant Formulae

[Content Not Disclosed]

Appendix E: Toxicity Testing Support Documents

1. Toxicity Testing Protocol
2. History of CROSERF
3. Solution Preparation Data Sheet