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Report on Patent and Literature Review on Dispersants



Kill Spill

Integrated solutions for combating marine oil spills

This project is supported by the European Commission under the Food, Agriculture and Fisheries and Biotechnology theme for the 7th Framework Programme for Research and Technological Development - Grant agreement 312139

Work package	WP1 In depth analysis of current knowledge and identification of technological gaps
Deliverable no	D1.3
Deliverable title	Report on Patent and Literature Review on Dispersants
Due date:	Month 12
Actual submission date:	2014-02-06
Start date of project:	2013-01-01
Deliverable Lead Beneficiary (Organisation name)	EcoTechSystems s.r.l.
Participant(s) (Partner short names)	GCL, UB, ICTP, Ecots
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Dissemination Level: (Public, Restricted to other Programmes Participants, REstricted to a group specified by the consortium, COntidential only for members of the consortium)	PU
Deliverable Status:	Final version



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1 Overview

Dispersants are a group of chemicals designed to be diffused onto oil slicks to accelerate the process of natural dispersion. In oil spill response, the use of dispersants is one of the more common approaches to reduce environmental impacts. The aim of use of dispersants is to move the oil into the water column, in order to allow its rapid dispersion and dilution. If not effectively dispersed, oil on the water surface could rapidly come into direct contact with marine biota; it will also continue to mix into the top meter of the water column and resurface for an extended duration. A fast dispersion of the oil could ideally reduce the exposure time of marine organisms to the oil.

Dispersants are capable of rapidly removing large amounts of certain oil types from the sea surface by transferring it into the water column. Following dispersant application, wave energy will cause the oil slick to break up into small oil droplets that are rapidly diluted and subsequently biodegraded by micro-organisms occurring naturally in the marine environment.

They can also delay the formation of persistent water-in-oil emulsions. In common with other response techniques, the decision to use dispersants must be given careful consideration and take into account oil characteristics, sea and weather conditions, as well as surrounding environmental sensitivities.

In certain situations, dispersants may represent the only means of removing significant quantities of surface oil quickly, in the attempt of minimising damage to marine resources. However, in common with all spill response options, the use of dispersants has limitations and its use should be carefully planned and controlled. Dispersant use will also depend upon national regulations governing the use of these products.

Many investigations have been conducted on the use of dispersants on surface oil spills, about their effectiveness and toxicity. By the results of these studies, it can be concluded that dispersants could represent an effective tool in mitigating coastal impacts, but only if applied under the appropriate conditions (Camilli et al., 2010) in order to minimize their impact on marine environment, which in some cases could be higher than that of the oil itself.

Besides the effectiveness of dispersants in reducing the visible oil spill environmental impact, the intrinsic toxicity of dispersant itself and the toxicity of dispersed oil should be taken into account. Modern oil spill dispersants have been assessed by standard toxicity testing techniques, revealing a higher eco-compatibility than the older formulations, at least less acutely toxic than the spilled oils that they are used to disperse (EMSA, 2010).

No large-scale applications of dispersants in deep water had been attempted prior to the Deepwater Horizon oil spill and thus a very low amount of data exists on the effectiveness of dispersant components released in the deep subsurface (Kujawinski et al., 2011).

In the next paragraphs, the main information about effectiveness, use and toxicity of commercial dispersant formulations are provided.

Within the European Union, a recent inventory of national practices and policies relating to the use of dispersants as an oil spill response tool, which was undertaken by the European Maritime Safety Agency (EMSA), has revealed a divergence of opinion amongst EU Member States (EMSA, 2005). In most States, the use of dispersant is secondary to mechanical containment and recovery, and in several states the use of dispersants is either not allowed or is highly restricted, particularly in the Baltic States. In other countries where dispersant use is permitted, in practice, they have not been used for a decade or more.



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2 Chemical dispersion

An oil slick can disperse effectively by natural dispersion, which occurs when waves and other turbulence at the sea surface cause all or part of the slick to break up into droplets and enter into the water column. The addition of chemical dispersants is intended to accelerate this natural process (Delvigne & Sweeney, 1988; Lessard & DeMarco, 2000)

Dispersants are commonly composed of two main molecular classes: surfactants and solvents. Because of their dual nature, the surfactant molecules in oil spill dispersants reach their lowest energy state by positioning themselves at oil–water interfaces, thereby lowering the oil-water interfacial tension and significantly lowering the energy required to generate oil droplets in water.

In addition, droplets generated with dispersants are typically much smaller than would otherwise form by the natural energy of the sea.

2.1 The dispersant action

Dispersants can be used neat (undiluted), in order to enhance their effectiveness, or in aqueous carrier systems. When they are sprayed onto an oil slick, the solvent (if present) will transport and distribute the surfactants through the oil slick to the oil/water interface: the dispersant droplets penetrate and mix into the oil slick, aided by the action of the solvent and the momentum of the droplet spray (Cormack et al., 1987). As dispersant reaches the lower part of the oil slick, the surfactant molecules spread along the oil–water interface and lower the interfacial tension (Fiocco & Lewis, 1999). The reduction on the surface tension at the oil/water interface allow small oil droplets in which the oleophilic part of the molecule is in the oil and the hydrophilic part is in the water. Small droplets of oil then begin to break away and disperse into the upper zones of the water column. As surfactant is carried off with the oil droplets, additional surfactant in the oil phase replenishes the slick oil–water interface. Thus, the oil slick tends to be gradually depleted as droplets break away and more surfactant reaches the interface. The dispersed oil droplets are stabilized by the surfactant layer which prevents coalescence and resurfacing. The larger droplets may rise back to the surface some will remain in suspension and will drift apart and become degraded by naturally occurring bacteria. If dispersion is successful, a characteristic brown plume will spread slowly down from the water surface a few minutes after treatment (Fiocco & Lewis, 1999). Figure 1 illustrates the action mechanism of dispersion.

Neat dispersant drops in the 300–800 μm range are generally considered to be optimum for application efficiency and coverage of the slick. Finer droplets can be blown off-target by winds, and larger droplets may break through the oil slick too rapidly, without mixing efficiently into the oil slick. Dispersant formulations with more oleophilic characteristics will more readily coalesce and mix with the oil slick, thus providing a higher overall application efficiency. Water-based carrier systems tend to be less effective due to their lower affinity to the oil slick and consequent loss to the sea water, and are generally most effective on freshly spilled and low viscosity oils.

Thus, the process of dispersion can be divided in two stages: the formation of oil droplets in the water column from the surface slick, and advection of these droplets by near-surface turbulence down into the water column to prevent resurfacing. By Stoke's law, smaller oil droplets rise more slowly than large droplets (Lee et al., 1981; Tklich & Soon Chan, 2002). Thus, conditions that result in increased near-surface turbulence and generate a greater number of smaller oil droplets produce faster dispersion rates (Lunel, 1993).

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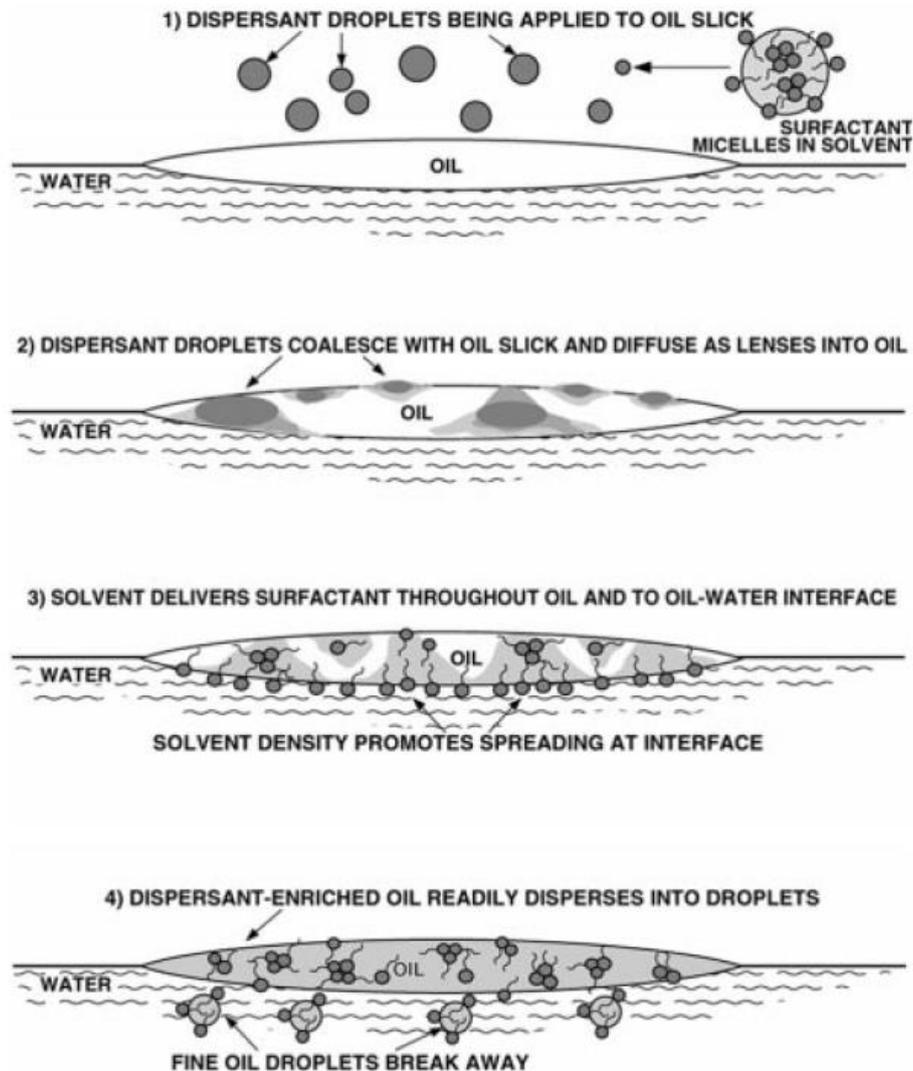


Figure 1: Mechanism of chemical dispersion. From Fiocco & Lewis, 1999.

2.2 Ways of application

2.2.1 Vessel spraying

Dispersants can be applied to open water by a variety of methods (EMSA, 2010). In general workboats are more suitable for treating minor spills in harbours or confined waters. Dispersants are usually applied by spray arms. In a typical spray arm system, pumps are used to pump dispersants from a storage tank through a set of nozzles calibrated to produce a uniform spray pattern of droplets. Ship spray arms are made as long as possible, consistent with the strength of the material used to manufacture them or consistent with the complexity of rigging systems required to support them. Large ships can have individual spray arms up to 12 m long (producing an overall spray width of nearly 30 m). Small boats have smaller spray arms, typically 5 or 6 m long (Fiocco & Lewis, 1999). Spray units can be portable or permanently installed on a vessel and systems are available which deliver the dispersant either undiluted or diluted with sea water. Spray arms are usually mounted as far forward on the vessel as possible to avoid the effect of the bow wave which can push the oil beyond the spray swath. Mounting the spray arms on the bow allows the vessel to travel faster and,



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because freeboard area is often greater at the bow also allows for longer spray arms. This combination allows optimization of the amount of oil which can be treated (increasing the encounter rate) with a limited dispersant payload. If spray arms are not available, fire hoses or monitors are sometimes used to apply diluted concentrate dispersants (Major et al., 1993). However, optimum dilution of the dispersant is difficult to achieve because of the very high flow rates and wastage of dispersant is a common problem. The high-powered jet of water also makes it difficult to apply the dispersant as a uniform spray of droplets and it frequently pierces through the oil making it ineffective. Thus fire monitors are unlikely to be an effective application tool unless specially modified for the purpose (Major et al., 1993).

Vessels offer certain advantages for dispersant spraying because they are usually readily available, easy to load and deploy, have cost advantages over aircraft and can apply dispersant fairly accurately to specific areas of a slick. Nevertheless, they also have serious limitations, particularly for larger spills, because of the low treatment rate which they offer and the added difficulty of locating the heaviest concentrations of oil from the bridge of a vessel. Furthermore, when slicks become fragmented or form narrow windrows, it is inevitable that some dispersant will be sprayed onto clear sea. These problems can be partially overcome by controlling the operation from spotter aircraft.

2.2.2 *Aerial spraying*

Dispersants can be also applied by airplanes or helicopters. Large multi-engine planes are best equipped for handling large off-shore spills. Small, single-engine aircrafts and helicopters are suitable for treating smaller spills and near shore areas (Martinelli, 1980).

The spraying of dispersant from an aircraft has the significant advantages of rapid response, good visibility, high treatment rates and optimum dispersant use. In addition, aircraft allow treatment of spills at greater distances from the shore than with vessels.

Two categories of aircraft are used: those designed for agricultural or pest control operations which require minor modification for dispersant application, and those which have been specifically adapted for the application of dispersant. Several types of helicopter have also been adapted to spray dispersants although most are able to carry an under slung bucket spray systems without the need for modifications. The ideal aircraft will be determined primarily by the size and location of the spill, although in reality local availability will be the crucial factor. The endurance, fuel consumption, turn around time, payload and the ability to operate from short or improvised landing strips are all important. In addition, the aircraft should be capable of operating at low altitude and relatively low speeds (50-150 knots) and be highly manoeuvrable.

Only type 3 dispersants are suitable for aerial spraying, since they require no mixing beyond that provided by the natural movement of the sea. The relatively low dose rate required also makes the best use of available payload.

2.2.3 *Shorelines applications*

Dispersants are sometimes used to remove oil from hard surfaces such as rocks, sea walls and other manmade structures, particularly during the final stages of clean-up. However, it is important to remove the bulk of the stranded oil by other means first. Shores subjected to strong wave action are often cleaned naturally and they should not be sprayed unless the oil has to be removed immediately.

Dispersants may be applied to the surface and scrubbed into the oil before flushing with sea water. The dispersed oil cannot be collected and for this reason dispersant use on the shoreline is restricted to areas of low environmental concern. Shoreline cleaners may also be used but it is important to note that their mechanism of action is different from that of dispersants. Degreasers are often carried on board ships to deal with small spillages of oil on deck but most are more toxic than



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dispersant and should not be used as a dispersant at sea or as a shoreline cleaner. Today it is recommended to use citrus-based chemical cleaners as these usually have a lower environmental impact than traditional chemical cleaners.

2.3 Formulations of dispersants

Dispersants are liquid blends of two main components: surfactants (surface active agents) and solvents, designed to hasten breakup of oil slicks into fine droplets that disperse naturally in the sea. Although the exact compositions of most commercially available oil dispersants are proprietary, they typically contain a high percentage of one or more uncharged or charged anionic surfactants of different solubility (Hemmer et al., 2011). The surfactants, which represent the active components, are amphipathic molecules, characterized by an oleophilic section (with an attraction to oil) and a hydrophilic part (with an attraction to water) that act to decrease tension between the water and oil interface, stimulating the development of small oil-surfactant micelles (National Research council, 2005; Singer et al., 1996). The non-polar, hydrophobic part is frequently a hydrocarbon chain. The polar component appears in many variations (Georgiou et al. 1992; Banat et al., 2000).

The surfactants used in modern dispersants are generally blends of non-ionic and anionic types (Rempec, 2011), including different kinds of molecules:

- non-ionic surfactants: sorbitan esters of fatty acids, sorbitan esters of oleic or lauric acid, polyalkoxylated sorbitan esters of fatty acids, polyalkoxylated fatty alcohols, polyethylene glycol esters of oleic acid, tall oil esters, ethoxylated sorbitan esters of oleic or lauric acid, polyethylene glycol esters of oleic acid, ethoxylated and propoxylated fatty alcohols, ethoxylated octylphenol.
- anionic surfactants: salts of dialkyl sulfosuccinates and of alkyl benzene sulfonic acid, sodium dioctyl sulfosuccinate, sodium ditridecanoyl sulfosuccinate. The anionic surfactant, dioctyl sodiumsulfosuccinate (DOSS), is a component of some of the most diffused dispersants, as Corexit 9527 and 9500.

Specific examples of surfactants used are: sorbitan monolaurate, ethoxylated sorbitan trioleate, ethylene/propylene oxide condensates, ethoxylated tridecylphosphate, sodium dioctyl sulfosuccinate, sodium lauryl sulfate, and isopropylamine dodecyl benzene sulfonate.

The most common non-ionic surfactants are ethoxylates, ethylene and propylene oxide co-polymers and sorbitan esters. Examples of commercially available ionic surfactants include fatty acids, ester sulphonates or sulphates (anionic) and quaternary ammonium salts (cationic). An alternative to the described chemical surfactants is represented by biosurfactants (Box 1). These compounds, mainly of microbial origin, belong to various classes, including glycolipids, lipopeptides, phospholipids, polysaccharide-lipid complexes, and hydroxylated cross-linked fatty acids. Their main advantages over synthetic chemical surfactants are their reduced toxicity, biodegradability, and production by simple processes. Substrates such as *n*-alkanes, vegetable oils and carbohydrates, or even industrial waste products can be used in their production. Biosurfactants are not derived from petroleum, which becomes increasingly important as petroleum prices increase (Marg, 1993). The advance in biotechnology and the emergence of more stringent laws have led to biosurfactants being a potential alternative to the chemical surfactants available on the market (Banat et al., 2000; Henkel et al., 2012) and an interesting perspective for future developments of dispersants.



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BOX 1: Biosurfactants

Microbial compounds which exhibit particularly high surface activity and emulsifying activity are classified as biosurfactants. Biosurfactants are structurally diverse compounds, mainly produced by hydrocarbon-utilizing microorganisms which exhibit surface activity (Banat et al., 2000). Biosurfactants are usually classified based on their biochemical nature and the microbial species producing them. Five major classes of biosurfactants are: (1) glycolipids, (2) phospholipids and fatty acids, (3) lipopeptide/lipoproteins, (4) polymeric surfactants, and (5) particulate surfactants (Parra et al., 1989; Desai & Desai, 1993; Nabholz et al., 1993).

Biosurfactants can be produced using relatively simple and inexpensive procedures and substrates (Kosaric 1992; Lang & Wullbrandt 1999; Makkar & Cameotra 1999). Some structural types of surfactant are produced using biological systems and cannot easily be synthesized by chemical processes (Gerson and Zajic 1979). These molecules can be tailor-made to suit different applications by changing the growth substrate or growth conditions (Fiechter 1992). Biosurfactants are both biodegradable, which is a positive ecological aspect (Zajic et al. 1977; Shoham et al. 1983; Oberbremer et al. 1990; Kesting et al. 1996) and non-toxic or less toxic than chemical surfactants (Poremba et al. 1991, b; Van Dyke et al. 1991; Flasz et al. 1998). They occur naturally in soil, which makes them acceptable from a social and ecological point of view. There are many potentially useful biosurfactants, including both ionic and non-ionic surfactants which range from short fatty acids to large polymers.

Solvents are compounds added to dispersants in order to dissolve solid surfactants, to reduce the viscosity of the product thus enabling uniform application, to enhance the solubility of the surfactant in the oil and/or to depress the freezing point of the dispersant.

Solvents may be divided in 3 main groups: (a) water, (b) water miscible hydroxy compounds and (c) hydrocarbons. Hydroxy compounds used in dispersant formulations include ethylene glycol monobutyl ether, diethylene glycol monomethyl ether and diethylene glycol monobutyl ether. Hydrocarbon solvents used in modern dispersants include odourless, low aromatic kerosene and high boiling solvents containing branched saturated hydrocarbons.

A frequent approach used to formulate the blend of surfactant components is based on the hydrophilic-lipophilic balance (HLB) system (Becher, 1957). This system uses a coding scale ranging from 0 to 20, based on solubility characteristics of the dispersant in water and oils. Lower HLB values are predominantly soluble in the oil phase and higher HLB values are predominantly soluble in the water phase. The surfactants are blended to an optimum dispersant HLB value (typically 10–11); in general, blends are more effective than a single surfactant at a given HLB value. While not thermodynamically rigorous, nor universally used, this approach can provide a useful starting basis for developing improved dispersant product formulations.

The solvent content of a dispersant has many important functions. First, of course, it must solubilize the blend of surfactant components and yield a liquid viscosity suitable for the various dispersant application systems. Secondly, it must penetrate into the oil when applied, and assist in the diffusion of surfactants through the oil slick to the oil–water interface. Solvents used in modern dispersants include oxygenated compounds such as glycols and glycol ethers and petroleum-derived nonaromatic hydrocarbons. Specific examples include ethylene glycol monobutyl ether, dipropylene glycol monomethyl ether, de-aromatized kerosene and isoparaffinic solvents, some of which are also used in cosmetics and household cleaners. Components such as alcohols and water are sometimes used as cosolvents or cosurfactants to help solubilize the surfactants and modify viscosity.

Exact compositions for commercial dispersant formulations are proprietary, but their generic chemical characteristics are broadly known (e.g., Wells et al., 1985; Brochu, et al., 1986; National Research Council, 1989; Fingas et al., 1990; Singer et al., 1991, 1996; George-Ares and Clark, 2000). In



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general, a limited number of surfactant agents are currently used. Current dispersant formulations consist of mixtures of one or more surfactants, which may be either non-ionic or anionic. Cationic (positively charged) surfactants are not used in current formulations (Clayton et al., 1993) because they are usually quaternary ammonium salts that are inherently toxic to many organisms.

The Corexit products (Corexit 9527 and Corexit 9500, which includes the same surfactants incorporated into a different solvent, George-Ares & Clark, 2000) contain a mixture of non-ionic (48 percent) and anionic (35 percent) surfactants. The major non-ionic surfactants include ethoxylated sorbitan mono- and trioleates and sorbitan monooleate; the major ionic surfactant is sodium dioctyl sulfosuccinate (Singer et al., 1991). Neither Corexit product contains polyethoxylated alkylphenols (J. Clark, ExxonMobil Research and Engineering Company, Fairfax, Virginia, written communication, 2004). A different solvent was used in Corexit 9500 for two reasons. First, prolonged exposure to Corexit 9527 caused adverse health effects in some responders. These effects were attributed to its glycol ether solvent (2-butoxyethanol). Therefore, the solvent was replaced by a mixture of food-grade aliphatic hydrocarbons (Norpar 13; *n*-alkanes ranging from nonane to hexadecane) in Corexit 9500 (Varadaraj et al., 1995). The second reason for changing the solvent in the reformulated dispersant was to extend the window of opportunity for dispersant use. This window of opportunity is limited by the effects of weathering on the chemical and physical properties of the spilled oil, especially the increase in oil viscosity. Corexit 9500 has been shown to be slightly more effective with high-viscosity oils than Corexit 9527.

The composition of dispersant products has evolved in the last 40 years. Early generations of acceptable dispersants were either water-based surfactant systems or nonaromatic hydrocarbon solvent-based systems (Fiocco & Lewis, 1999; Abdel-Raouf, 2012). These generally required high application rates, e.g. a 1:3 dispersant: oil ratio (DOR), and additional mechanical agitation, such as by ship propellers, fire monitors or 'breaker boards.' Modern dispersants use solvent systems that allow much higher surfactant content ranging up to about 65% surfactant. These modern 'concentrate' dispersants therefore are effective at lower application rates, e.g. 1:20 DOR or less. For example, at breaking wave sea conditions, application ratios of less than 1:100 DOR can be adequate for effective dispersion with a 'concentrate' dispersant (Mackay, 1995). Additional information on the three main dispersants generations are reported in the next paragraphs.

2.3.1 *First generation "dispersants"*

The first oil spill dispersants, used since the 1960s, were essentially industrial detergents developed for other uses, such as industrial cleaning or washing vehicles (EMSA, 2010). They were hydrocarbon-based and were made of aromatic hydrocarbons, which gave rise to toxic effects (Lindgren et al., 2001). They represented a variety of different surfactants dissolved in solvents, occasionally used to clean up spilled oil on a small-scale. Only in the *Torrey Canyon* oil spill in 1967, industrial detergents were used to treat an oil spill on a large scale. About 10,000 tons of detergents were used to try and clean the estimated 14,000 tons of spilled oil off of the beaches in Cornwall in the UK, with a massive damage to the local environment. The use of dispersants at the *Torrey Canyon* oil spill demonstrated that their toxicity was much too high and that devastating impact on marine life outweighed their efficiency as pollution clean-up agents (Rempec, 2011).

2.3.2 *Second generation dispersants or "Conventional" oil spill dispersants*

The first formulations of surfactants and solvents specifically designed for use as oil dispersants at sea, were developed in conformity to the requirements of the UK regulations introduced in 1971 as a response to the *Torrey Canyon* oil spill. The UK regulations specified an acceptable level of toxicity, a minimum level of effectiveness and the required physical properties.



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The essential difference between the first and the early second generation oil spill dispersants was the use of hydrocarbon solvents with a much lower amount of aromatic hydrocarbons, as benzene, toluene, ethylbenzenes and xylenes (BTEX), thus resulting in a lower a lower toxicity to marine life. The solvent in most of these dispersants was “odourless”, “non-aromatic” or “low-aromatics” kerosene. They typically contained 10% to 25% weight of a surfactant of the fatty acid ester type. In the UK, this type of dispersant was categorized as “UK Type 1”, “Hydrocarbon-base” or “Conventional” oil spill dispersant. These “Conventional”, “Hydrocarbon-base”, or “UK Type 1” dispersants were recommended for use at 1 part of dispersant to 2 - 3 parts of spilled oil. This is a very high treatment rate, requiring 30% to 50% of the spilled oil volume to be added as dispersant. The need to use so much dispersant on the spilled oil presented a high amount of logistic disadvantages, leading to the formulation of new and concentrated dispersants (Third generation dispersants).

2.3.3 *Third generation dispersants or “Concentrate” oil spill dispersants*

These dispersants contain a higher amount of surfactant (up to 50% weight) than the “hydrocarbon-base” dispersants. The solvent is glycol ether solvent instead of kerosene (EMSA, 2010; Rempec, 2011). Because of the higher surfactant content, these “Concentrate” or “Water-dilutable” dispersants generally have a much higher viscosity than the “Hydrocarbon-base” dispersants.

These dispersants are usually diluted with seawater in order to allow the use of conventional spraying equipments. In the UK, a distinction was needed to distinguish this type of dispersant from the “Conventional” or “Hydrocarbon-base” dispersants and this type of dispersant was designated as “Concentrate, Water-dilutable” or “UK Type 2”, oil spill dispersant.

However, the dilution of the dispersant with seawater reduces the efficiency of the dispersant, especially when the dispersibility of the spilled oil is low. Additionally, the “UK Type 2” dispersants were effective when used undiluted at a much lower treatment rate than had previously been recommended.

The dispersant was recommended to be used at a treatment rate of 1 part of the seawater plus dispersant mixture (90% volume seawater + 10% volume dispersant) to 2 - 3 parts of spilled oil. This was the same high treatment rate as the UK Type 1 dispersants, except that the dispersant was used as a mixture of 10% volume “concentrate” dispersant (containing all the surfactants plus some solvent) and 90% volume of seawater acting as an additional solvent.

The UK introduced a third type classification of dispersants: “Concentrate” or “UK Type 3” dispersant. This type of dispersant is recommended for use at a treatment rate of 1 part of dispersant to 20 to 30 parts of spilled oil. Practical experience has shown that a dispersant treatment rate of 1 part dispersant to 10 or 20 parts of spilled oil is often needed, although lower treatment rates, such as 1 part dispersant to 50 parts of spilled oil, or even 1 part of dispersant to 100 parts of spilled oil, can be effective with low viscosity oils.

Since these dispersants could only be sprayed by aircrafts, dispersant manufacturers have subsequently developed formulations that can be sprayed from both boats and ships with water dilution (as a UK Type 2 dispersant), or sprayed undiluted (as a UK Type 3 dispersant) also from boats and ships. Many of these dispersants available today are therefore classified as “Concentrate” dispersants or in the UK as “UK Type 2/3 Concentrate” dispersants.

In table 1 are summarized the overall characteristics of dispersants described above.

The table 2 summarizes the main features of formulations of dispersants type1, 2 and 3.



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Table 1: Types of commercial dispersants currently available

Description and Generation	UK Type	Sprayed from	Recommended treatment rate	Comments	Current Availability
1st generation dispersants	-	Ships, onshore boats,	High treatment rate 30 - 50% dispersant as volume of spilled oil or 1 part dispersant to 2 to 3 parts oil	Industrial detergents with solvents that are too toxic to be used to be used as dispersants	No longer used as oil spill dispersants
“Conventional” or “Hydrocarbon-base” or “2nd generation dispersants”	UK Type 1 “Conventional” or “Hydrocarbon-base” dispersant	Ships, onshore boats,	High treatment rate 30 - 50% dispersant as volume of spilled oil or 1 part dispersant to 2 to 3 parts oil	Low toxicity	Available
“Concentrate” or “3rd generation dispersants”	UK Type 2 “Water-dilutable concentrate dispersant	Ships and boats	High treatment rate 10% solution of dispersant in seawater to 2 to 3 parts oil Equivalent to 1 part dispersant to 20 to 30 parts oil	Low toxicity when diluted with water and can only be sprayed from ships and boats in this way.	Available
	UK Type 3 “Concentrate” dispersant	Aircraft, ships and boats	Low treatment rate 3 to 5% dispersant as volume of spilled oil or 1 part dispersant to 20 to 30 parts oil	Low toxicity Used undiluted (or ‘neat’)	Available



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Table 2: Typical compounds used in dispersant formulations (from Rempec, 2011)

Generation	Description	UK Type	Surfactants	Solvents
First	Industrial detergents	-	Various compounds	Aromatic hydrocarbons
Second	Hydrocarbon-base, Conventional	Type 1	(i) Fatty acid esters (ii) Ethoxylated fatty acid esters	Light petroleum distillates: Odourless or de-aromatised kerosene Low aromatics (less than 3% wt.) kerosene CAS No. 64742-47-8 EC No. 265-149-8
Third	Water-dilutable concentrate dispersant	Type 2	(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	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
	Concentrate dispersants	Type 3	(iii) Sodium di-iso-octyl sulphosuccinate EC No. 209-406-4 CAS No. 577-11-7	Light petroleum distillates: Hydrotreated light distillates CAS No 64742-47-8 EC No. 265-149-8

2.4 Effectiveness of dispersants

Dispersant effectiveness is defined as the amount of oil that the dispersant puts into the water column compared to the amount of oil that remains on the surface. (Fingas & Ka’aihue, 2004). Effectiveness remains a major issue with oil spill dispersants. Many factors influence dispersant effectiveness, including oil composition, sea energy, state of oil weathering, the type of dispersant used and the amount applied, temperature, and salinity of the water (Canevari, 1985; Nichols & Parker, 1985; Moles et al., 2001; Fingas & Ka’aihue, 2004; National Research Council, 2005). The most important of these is the composition of the oil, followed closely by sea energy and the amount of dispersant applied. It is equally important to recognize that the only thing that matters in the end is effectiveness on real spills at sea.

2.4.1 Oil characteristics

In determining the effectiveness of dispersants, the chemical composition and the application system are among the main influencing factors. Other important factors are represented by the composition and state of the oil being dispersed, the ratio of dispersant to oil, and the amount of mixing energy in the system. Oil composition can vary considerably, from light crude oils which will evaporate to a significant degree, to medium crude oils with different amounts of aromatics, saturates, resins and asphaltenic and polar compounds, to heavy crude oils and fuel products with lower volatility and higher viscosity (Fiocco & Lewis, 1999).

Oil viscosity is an important parameter in the dispersant effectiveness. Oil-water emulsification result in a significant increase in volume and viscosity (Xie et al. 2007). Dispersants usually have little effect on very viscous, floating oils, as they tend to run off the oil into the water before the solvent can penetrate (Cheremisinoff & Davletshin, 2010). As a consequence, some oils are more amenable to dispersion than others: during the UK 2003 sea trials (Lewis, 2004) the IFO 180 that was used in the trial dispersed much more readily than the IFO 380. As a general rule, dispersants are capable of dispersing most liquid oils and emulsions with viscosities of less than 2000 centistokes (SL Ross Environmental Research & MAR Inc., 2006) equivalent to a medium fuel oil at 10-20°C. They are unsuitable for dealing with viscous emulsions (mousse) or oils which have a pour point near to or above that of the ambient temperature (Cheremisinoff & Davletshin, 2010). Moreover, even those oils which can be dispersed initially become resistant after a period of time as the viscosity increases as a result of evaporation and emulsification. For a particular oil, the time available before dispersant stops being effective depends upon such factors as sea state and temperature but is unlikely to be longer than a day or two. Dispersants can, however, be more effective with viscous oils on shorelines because the contact time may be prolonged allowing better penetration of the dispersant into the oil.

2.4.2 Weather and sea state

As weathering will increase the viscosity of the oil, it therefore follows that the longer the oil is left to weather, the less likely it is to disperse effectively (Chapman et al., 2007). Other properties of oil, such as asphaltene and wax content, also affect the behaviour of oil spilled at sea and the manner in which it will weather, emulsify and disperse (Strom-Kristiansen et al., 1997). Knowledge of oil properties and how they change with weathering is therefore important in determining whether or not dispersants should be used during a real incident.

Sea state and weather conditions play an important role in the dispersion of oils at sea. Laboratory tests by means of wave tank approach) and field studies resulted in better dispersions coupled with higher energy mixing (Lewis, 2006; Mullin & Trudel, 2006; Chapman et al., 2007). It is often reported that wind speeds of at least 5 m/s are needed to generate enough wave energy for good dispersion;



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otherwise, dispersants are ineffective in calm conditions (National Research Council, 2005) and without a possibility of wave energy increase within a reasonable timescale (Nedwed et al., 2006). On the other hand, in windy conditions and bad sea state, it is difficult to accurately target the oil, which may be overwashed by waves thereby inhibiting the interaction between the dispersant and oil. Any dispersant that does hit the oil is likely to be washed or blown off into the sea before it has a chance to penetrate to the oil-water interface and to have any effect.

The incident involving the NATUNA SEA in the Singapore Straits in 2000 serves as a good example of the importance of having information on the oil properties and weather conditions at the time of an incident. When some 7000 tons of Nile Blend crude oil were spilled from the vessel as a result of the grounding, dispersant was applied to thick oil patches around the stricken vessel. No previous testing had been carried out to assess dispersant effectiveness on this little known crude oil but visual observations showed that the oil was semi-solid as early as the first day after the spillage. When the properties of the oil were evaluated in more detail, it was found that the sea temperature was 3°C below the pour point of the oil and the viscosity was estimated to be greater than 50,000 mPa and beyond the envelope of effective dispersion. The situation was further exacerbated by calm weather conditions where there was little wave energy to promote effective dispersion. In situ fluorometry was used to monitor the effectiveness of dispersion and the results verified the visual observations and predictions based on the oil properties, supporting the conclusion that the oil was not amenable to chemical dispersion.

This is in contrast to a recent incident in adjacent waters in which fresh IF0380 leaking from a container vessel's fuel tanks was successfully treated with dispersant because the oil was relatively light, and the warm waters helped to keep it sufficiently fluid to allow penetration of the surfactants.

2.4.3 *Salinity*

The major commercially available dispersants have been formulated for use in standard marine salinities, i.e. ~30‰ or higher. Some studies demonstrated that their effectiveness generally decreases at low salinities (Blondina et al., 1999; Chandrasekar et al., 2006). The effectiveness of a dispersant is a function of how much of the surfactant is available to reach the oil-water interface and reduce the interfacial tension: with the decrease of salinity, the surfactant solubility increases making the surfactant less available to interact with the oil.

Salinity is not a limiting factor only when the oil and dispersant were pre-mixed, with no significant changes with respect to droplet size or subsequent coalescence kinetics (Sterling et al. 2004). However, pre-mixing is not feasible in a real system. Therefore, in order to enhance the dispersant effectiveness in low salinity, the surfactant solubility lab trials have been performed increasing the salt content of the dispersant formulation by the addition of calcium chloride, thus lowering the dispersant solubility (George-Ares et al., 2001). The results indicated an improved effectiveness of products in brackish and fresh water. Currently, there are no statutory product approval schemes in Europe that assess product efficiency or toxicity under conditions of low salinity. For example, in the United Kingdom, both the efficacy test (Morris & Martinelli, 1983) and the toxicity assessment (Kirby et al., 1996) that are used to approve oil spill treatment products are carried out under full marine salinity conditions.

2.4.4 *Ratio of dispersant to oil*

In general, increasing the ratio of dispersant to oil (DOR) will increase the rate and degree of oil dispersion. A DOR of about 1:20 is generally suggested as a target for response planning purposes and is used in many standard laboratory effectiveness tests to compare dispersant performance. Typically, an average thickness of the area of oil slick to be treated with dispersant is assumed, e.g. 0.1–0.2 mm. To illustrate the application rate relationship, a 0.1 mm thick oil layer is equivalent to



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100 mL/m² (1000 L/hectare; 100 US gallons/acre) of oil and therefore requires the spray system to deliver 5 mL/m² (50 L/hectare; 5 US gallons/acre) of dispersant to achieve a DOR of 1:20 or 5% of the oil volume.

Slick thickness, in a real system, can vary over a wide range. Within the thickest areas of the slick, the average thickness ranges to several millimetres, and, in some cases, up to several centimetres. For example, when oil emulsifies, the wind and currents can cause it to concentrate in patches that are several millimetres thick. In other areas of the same oil slick, e.g. sheen, the oil layer thickness may only be a few microns. While the dispersant application rate can be set by the spraying ship or aircraft, the oil thickness can generally only be estimated. Thus the treatment ratio (DOR) actually resulting at a particular area of an oil slick is not precisely determinable. Thick areas of oil, e.g. emulsion, generally need to be treated using multipass dispersant spray applications to achieve the proper DOR.

Although DOR of 1:20 is a frequently targeted treatment rate for modern dispersants, it should be noted that freshly spilled, low viscosity crude oils can be effectively dispersed at lower treatment rates. Higher energy conditions will increase the rate of oil dispersion, or, alternatively, allow effective dispersion at lower DORs. Thus, depending on circumstances, the overall treatment ratio of dispersant used to oil dispersed at some spills can be lower than that normally used in laboratory tests. For example, DORs from about 1:60–1:100 were found to be effective at the Sea Empress spill (The Environmental Impact of the Sea Empress Oil Spill, 1998). On the other hand, for difficult-to-disperse oils, such as viscous or emulsified oils, greater DORs (e.g. up to about 1:5) may be needed for effective dispersion.

An important feature of dispersants is the ability to break water-in-oil emulsions that form naturally as the oil slick weathers and tosses about on the sea surface. Recent laboratory and field experiences have demonstrated the ability of some dispersants to break emulsions formed at sea, particularly before the extremely viscous and stable 'mousse' stage of emulsion forms (Lewis et al., 1995; Fiocco & Lessard, 1997). This demulsification activity promotes coalescence of the water droplets in the emulsion, which in turn causes separation of water and lowering of viscosity (Fiocco & Lewis, 1999). This step will slow down the dispersion process and can make effectiveness monitoring more difficult, since oil releases more slowly into the water column. In addition, since a portion of the dispersant can be used up in the demulsification step, application of additional dispersant may be needed to increase the dispersion rate (Fiocco & Lewis, 1999).

As mentioned, viscous difficult-to-disperse oils can require more than the typically targeted 1:20 DOR treatment. It should be noted that models for predicting the window of opportunity for dispersant use on a spill do not always account for specific differences between dispersants, such as the demulsification capability of the dispersant (Fiocco & Lewis, 1999).

BOX 2: efficacy of dispersants

Even though the set-up of dispersants chemical formulations improved the effectiveness of these products in the last decades, there are still evident technological gaps often limiting the use of these products in small time and weather windows. Future research should be devoted to set up products with enlarged range of oil types, possibly including heavy and viscous oils which to date represent the more refractory targets for commercial dispersants. This will allow, as a consequence, enlarging the weather window of opportunity of dispersants. Future developments should be made towards dispersants less dependent to water salinity, and thus available for use also in brackish and fresh waters.

2.4.5 *Estimating the dispersant efficacy*

Effectiveness issues are confounded by the fact that various tests show highly different results depending on how they are constructed and operated. Detailed scientific examination of most of these shows major deficiencies. Emphasis should be on real results from real spills.

Many different types of procedures and apparatus for testing dispersants are described in the literature (Fingas, 2002; Fingas, 2008). However, only a handful of these are commonly used. The more common tests include:

- Warren Springs Laboratory (WSL; Labofina): 5 mL of oil is mixed with 250 mL of synthetic seawater in a conical separatory funnel. Dispersant is added to the oil surface dropwise, and the funnel is rotated end-over-end at 34 ± 2 rpm for five minutes. After mixing stops, the oil-water dispersion is allowed to stand for one minute to allow large oil droplets to rise, and a 50-mL sample is removed through the stopcock at the bottom. The oil in the sample is extracted into methylene chloride and the oil concentration is determined by measuring the absorbance at 580 nm (National Research Council, 2005).
- Swirling Flask Test: 0.1 mL of oil is added to 120 mL of synthetic seawater in a modified 125-mL Erlenmeyer flask. Dispersant may be either premixed with oil (Sorial et al., 2001) or added to oil floating on the water surface (Blondina et al., 1997; Venosa et al., 1999). The flasks are mixed by swirling at 150 rpm on a gyratory shaker table, and then allowed to settle for 10 minutes before a sample of the aqueous phase is collected by pouring through a glass spout that extends from the bottom of the flask upward to the neck. The oil concentration is estimated measuring absorbance of long-wave ultraviolet light by methylene chloride extracts of the aqueous samples or by means of gas chromatographic analysis.
- Baffled flask test: same method described for swirling flask test, but using a modified 150-mL trypsinizing flask that contains a stopcock near the bottom of the flask. Measurements of the absorbance of methylene chloride extracts are performed at different wave lengths.

These tests have different reliabilities. Results of the effectiveness for a single product can strongly differ among the experimental approaches (Table 3).

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Table 3: Comparison of Laboratory and field test Effectiveness results (from Lunel et al. 1995)

Oil Type	Dispersant	Field test	SF	SF	IFP	WSL	WSL	Exdet
			GC	GA		Lab1	Lab2	
Medium fuel oil	Corexit 9527	26	54	50	91	42	42	67
Medium fuel oil	Slickgone NS	17	49	46	94	29	23	50
Medium fuel oil	LA 1834/Sur	4	2	2	50	16	11	38
Forties crude	Slickgone NS	16	47	65	95	28	25	60
Forties crude	LA 1834/Sur	5	2	2	61	15	12	53
Correlation with field test (R²)			0.89	0.7	0.54	0.87	0.94	0.41
Ratio Lab/field test			0.4	0.35	0.19	0.56	0.62	0.27

Effectiveness Results in Percent

Legend SF= Swirling Flask, GC= analysis by Gas Chromatography, CA= Colorimetric analysis

IFP= French Institute for Petroleum test, WSL= Warren Spring Laboratory Test

BOX 3: reliability of efficacy tests and applicability of results to real systems

The measurement of effectiveness of dispersants in the laboratory is easier than in the field; however, only few standard testing procedures are available and generally accepted. Moreover, the results obtained with different tests can differ considerably one from the other. Finally, laboratory conditions usually don't replicate the complexity of real systems, thus affecting the reliability of results. To date, while all commercial dispersants are widely tested in laboratory, there is a lack of information about their field effectiveness. All historical tests relied heavily on developing a mass balance of oil in the water column and that left on the surface (Fingas, 2000), but there is no general consensus about what experimental approaches are most appropriate for field tests and for the evaluation of results. A better understanding of the relationship between the different testing regimes and the natural environment may enable more reliable predictions to be made during real incidents (Chapman et al., 2007). The quest for a method to quantify the amount of oil dispersed during the response to a real incident is still unfulfilled.

With the large variety of different crude oils and fuel oils that are carried on tankers transiting European waters, information from laboratory testing, sea trials and real incidents can be useful to enable decisions to be made rapidly and with greater confidence (Chapman, 2007). Where the properties of the oil are known in advance, such as during exploration and production or storage activities, testing of the oil under different conditions to optimise dispersant effectiveness should help decision making. For example, Norwegian pollution control authorities require testing to determine the characteristics and dispersibility for most of the oils in production in the North Sea and Norwegian Sea (SINTEF, 2005). This includes determination of the window of opportunity for effective dispersion of a particular oil. However, while testing in advance may be of use on a local scale, it would be impossible to test every single crude and refined oils produced worldwide, and under all possible conditions. In many spills therefore the properties of the oil and its amenity to dispersant treatment are unknown, and so in-situ dispersant spray trials early on in a spill can be used to determine whether the oil in question will disperse under conditions specific to that spill.

2.5 Dispersants toxicity and environmental compatibility

Assessment of the environmental impact of petroleum compounds on the marine environment is complicated because these products consist of complex mixtures of organic compounds. Following discharge of petroleum into the sea, between 2% and 5% of the organic components dissolves into the water phase (Payne et al., 1987). Dissolution and dispersion are important processes with respect



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to potential toxic effects of petroleum in the water column. The dissolved fraction appears to be the most available for the marine biota (Neff & Anderson, 1981), as studies have shown that the primary route of hydrocarbon uptake from the water is via the gills (Thomas & Rice, 1981).

The concentration of petroleum compounds in the water column can be greatly enhanced by the addition of dispersing agents. Chemical dispersants aid the dispersion of crude oil by reducing the oil/water interfacial tension, along with the natural motion of the sea, which allow the break-up of oil into very fine droplets (Gilbert, 1996). Because of their molecular properties of opposed solubility tendencies, surfactants present in the water column have the potential to interact with the cellular lipid membrane of the fish gills and alter the permeability of the cells and its organelles (Signer et al., 1995). This may cause a variety of physiological disturbances, ranging from subcellular to organism level.

The first products used for oil spill combating released a lot of petroleum compounds. For example, chemical cleaners used at the *Torrey Canyon* were toxic to marine life because they contained solvents composed of aromatic compounds, such as benzene, toluene and xylene. These solvents were especially suited for the primary purpose of these products; to remove oil, grease and dirt from surfaces such as dirty engines and garage floors. None of these components are used in modern dispersants; however, oils, particularly light distillate fuels, can contain a fair proportion of aromatic compounds. Although most of these rapidly evaporate, some will transfer into the sea where they may exert toxic effects, depending on the peak concentration reached. This can happen whether or not the oil is treated with dispersants. As an extreme example, the North Cape spill (Michel et al., 1997) of No. 2 fuel oil, used for domestic heating, demonstrated that oil with a high aromatics content, naturally dispersed by very rough seas into very shallow water, can exert narcosis-inducing or toxic effects, particularly to creatures such as lobsters and crabs. Dispersants were not and would not be recommended for this type of oil spill situation.

The assessment of dispersants ecocompatibility is a matter of methodological discussions. Laboratory experimentation, field trials, and monitoring of spills of opportunity have supplied much of what is currently known of the potential toxicological consequences of oil spills and oil spill response measures. However, all of these approaches have some disadvantages. Laboratory experiments, even though being standardized, cannot adequately address the scale or complexity of actual spills, with ecological interactions between biota and environment. Field studies to better simulate actual oil spill conditions are restricted by high costs, difficulties in replicating experiments, and regulatory restrictions. Mesocosm-scale tests have been proposed as a way to bridge the gap between laboratory and field studies for testing purposes (Coelho et al., 1999). However, mesocosms have been employed in only a limited number of such studies to date.

BOX 4: environmental compatibility of dispersants

The assessment of environmental compatibility of dispersants presents some important methodological gaps that make very difficult a correct comparison of the available data. Even though some steps have been made towards the standardization of laboratories toxicity testing methods, data garnered from long-term monitoring of field studies are still very poor. Moreover, besides the toxicity assessment, there is insufficient understanding about the fate of dispersants and dispersed oil in aquatic ecosystems, and particularly about interactions with the benthic compartment, the potential accumulation in sediments and subsequent effects on biotic components of exposed ecosystems. In addition, the relative importance of different routes of exposure, that is, the uptake and associated toxicity of oil and dispersants in the water column and their impact on the main component of the food web, is still poorly understood and not usually considered in impact assessment of new products.



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3 Commercial dispersants

3.1 Types of commercial dispersants

As stated in paragraphs 3.1-3.3, dispersants are classified basically into 3 classes: first, second and third “generations”. The 2nd and the 3rd generation are commonly called, respectively, conventionals and concentrates. Aside this classification, the UK authorities classified dispersants according to the generation and to the application method for which the product has been approved (Rempec, 2011):

- Type 1: conventional dispersants based on hydrocarbon solvents with between 15% to 25% surfactant. They are sprayed neat onto the oil as pre-dilution with seawater renders them ineffective. Typical dose rates are between 1:1 and 1:3 (dispersant:oil).
- Type 2: dispersants are dilutable concentrate dispersants which are alcohol or glycol (i.e. oxygenated) solvent based with a higher surfactant concentration. Dilution is normally 1:10 with seawater. Applied from boats.
- Type 3 dispersants are also concentrate dispersants with a similar formulation to type 2 products. However, they are designed to be used in neat form and typical dose rates are between 1:5 and 1:30 (neat dispersant:oil). Applied from boats or aircrafts.

Type 1 and 2 dispersants require thorough mixing with the oil after application to produce satisfactory dispersion. With type 3 products, the natural movement of the sea is usually sufficient to achieve this. The lower application rates required with concentrates mean that types 2 and 3 have largely superseded type 1 dispersants for application at sea.

In the following paragraph is provided a census of commercial dispersants patented, used or available for use in EU and USA.

3.2 Commercial dispersants in Europe and USA

Commercial dispersants have evolved in the last 30 years among the 3 types of dispersants described before, up to the “low toxicity oil spill dispersants” available today.

For example, the “Finasol” range, now marketed by Total, progressed from Finasol OSR 2 (a “Conventional”, “Hydrocarbon-base” or UK Type 1 dispersant), through improved versions of the same type of dispersant (Finasol OSR 3, 4, 7 and 12) to Finasol OSR 5 (a “Concentrate”, “UK Type 2/3 dispersant”). This was subsequently improved to produce Finasol OSR 51 and 52 and, most recently, Finasol OSR 61 and 62. All the dispersants are of the Finasol brand, but they cover the full range of generations and types of dispersants available.

All three types of dispersants are still available today:

- “Conventional”, “Hydrocarbon-base” or “UK Type 1” dispersants that can be useful in the minor role of shoreline clean-up
- “Concentrate Water-dilutable” or “UK Type 2” dispersants that can be sprayed from boats or ships.
- “Concentrate”, “UK Type 2/3” dispersants can be sprayed from aircraft and ships.

The salient points about the different generations and types of oil spill dispersants are presented in tables 1 and 2. Table 4 provides a list of patented dispersants in EU and USA. A list of commercial dispersants used in EU and USA waters is provided in Table 5.

The use of dispersants as an oil pollution response method at sea remains a widely discussed issue in the EU due to the above-mentioned environmental trade-offs. Following the widespread use of substantial amounts of dispersants during the response to the Deepwater Horizon incident in the Gulf of Mexico in 2010, one can expect new information on the environmental impacts and long-term effects of dispersant use. However, comprehensive information was not available at the time this document was prepared.

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Table 4: List of patented dispersants in EU and USA

NAME	COUNTRY	PATENT NO.	PUBLICATION DATE	DESCRIPTION
ACCEL CLEAN DWD	USA	US 8389459 B2	2013	Septic system cleaning compositions
		US 7658848 B2	2010	Septic system cleaning
		US 7659237 B2	2010	Increasing surface-active properties of surfactants
ATLANTOL AT7	Cyprus	US 5399350	1995	Proteinaceous oil spill dispersant
BIODISPERS	USA	US 6660698 B2	2003	Methods for extinguishing petroleum-based fires, suppressing petroleum-released vapours and cleaning petroleum-contaminated surfaces
		US 5753127 A	1998	Compositions and methods for dispersing and biodegrading spilled petroleum oils and fuels
		US 8093304	2012	Demulsification of water-in-oil emulsion
		US 8101086	2012	Oil/water separation of full well stream by flocculation-demulsification process
		US 8298997	2012	Core annular flow of heavy crude oils in transportation pipelines and production wellbores
		US 7008536	2006	Oil desalting and dewatering
		US 7108780	2006	Oil desalting by forming unstable water-in-oil emulsions
COREXIT 9500	France, USA	WO 2006074277 A1	2006	Surfactant combined flow through capacitor
COREXIT 9527	USA	WO 2003087263 A2	2003	Improvements in oil desalting by forming unstable water-in-oil emulsions
COREXIT 9600	Cyprus	WO 2003099962 A1	2003	Crude oil desalting method
		US 6168702 B1	2001	Chemical demulsifier for desalting heavy crude
		US 5672739	1997	Class of three tail surfactants law388
		EP 0696631 A2	1996	Demulsifier for water-in-oil emulsions and method of use
		WO 1996005272 A2	1996	Oil treatment and compositions therefor



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		US 4551239	1985	Water based demulsifier formulation and process for its use in dewatering and desalting crude hydrocarbon oils
DISPERSIT SPC 1000™	USA	US 6261463 B1	2001	Water based oil dispersant
		US 8092708 B2	2012	Composition for remediation of waste water
		US 7964100 B2	2011	Remediation of waste water
FFT-SOLUTION™	USA	US 20080169239 A1	2008	Remediation of waste water
		WO 2008089122 A3	2008	Remediation of waste water
		WO 2008089122 A2	2008	Remediation of waste water
ZI-400 (formerly TI-400 OIL SPILL DISPERSANT)	USA	EP 0598143 A1	1994	A cleaning, wetting agent and solvent
		CA 2081803	1994	Cleaning, wetting agent and solvent
		DE 4238424	1994	Purifying wetting and solvent

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Table 5: List of commercial dispersants used in EU and USA waters

PRODUCT	CHARACTERISTICS	EU COUNTRIES IN WHICH THE USE IS APPROVED
ACCEL CLEAN DWD	Unknown	USA
ATLANTOL AT7	Type 2/3	Cyprus
Agma DR 379	Type 2/3	UK
AGMA OSD 379 SUPER CONCENTRATE	Type 2/3	Cyprus
Agma OSD 569	Type 2	UK
BIODISPERS	Unknown	USA
BIOREICO R93	Unknown	France
BIOVERSAL HC	Type 2/3	Italy, Spain
BP ENERSPERSE 1583	Type 2/3	Cyprus
BS-300	Type 2/3	Spain
CAFLON OSD	Type 2/3	UK
CLEAN SEA ECO 83	Type 2/3	Italy
CHIMSPERSE	Type 2/3	Italy
COREXIT 9500	Type 2/3	France, USA
COREXIT 9527	Type 3	USA
COREXIT 9600	Unknown	Cyprus
DASIC SLICKGONE EW	Type 2/3	UK
DASIC SLICKGONE LTE	Unknown	Cyprus
DASIC SLICKGONE NS	Type 3	Cyprus, France, UK, Belgium
DISPEREP 12	Unknown	France
DISPER M	Unknown	France
DISPERSIT SPC 1000	Unknown	USA
DISPOIL	Unknown	France
DISPOLENE 36S	Unknown	France
EMULSOL LW	Type 1	UK
EMULGAL C-100	Unknown	Cyprus, France
F-500	Unknown	Italy
FFT-SOLUTION	Unknown	USA
FINASOL OSR 2	Unknown	Cyprus
FINASOL OSR 4	Unknown	Cyprus
FINASOL OSR 5 CONCENTRATE	Unknown	Cyprus
FINASOL OSR 7	Unknown	Cyprus
FINASOL OSR 12	Unknown	Cyprus
FINASOL OSR 51	Type 2/3	Cyprus, France, UK
FINASOL OSR 52	Type 2/3	Cyprus, France
FINASOL OSR 52 SR 52	Type 2/3	UK
FINASOL OSR 61	Type 2/3	France
FINASOL OSR 62	Type 2/3	France
FINASOL OSR 121	Unknown	Cyprus
GAMLEN OD 4000 (PE 998)	Type 2/3	Cyprus
GAMLEN OSR 2000	Unknown	Cyprus
GAMLEN OSR LTL26	Unknown	Cyprus
GARD SLICKSOL	Type 2/3	UK

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INIPOL IP 80	Unknown	France
INIPOL IP 90	Unknown	France
INIPOL IPC	Unknown	France
JD-109	Unknown	USA
JD-200	Unknown	USA
MARICHEM OIL SPILL DISPERSANT	Type 2/3	Greece
MARE Clean 200 (formerly MARE CLEAN 505)	Unknown	USA
MARINE D-BLUE CLEAN	Unknown	USA
NEOS AB3000	Unknown	USA
NEUTRALEX C	Unknown	France
NTI 53 E101 S.P. NAT B. STIM-1	Unknown	Italy
NU CRU	Type 2/3	France, UK
OCEANIA 1000	Unknown	France
OD 400	Type 3	Spain
OD 4000	Type 2/3	UK
OD 4000 (PE 998)	Unknown	France, UK
OILER 60	Type 2/3	Greece
OIL SPILL DISPERSANT/ NF	Type 1	Cyprus
OIL SPILL ELIMINATOR N/T	Unknown	Cyprus
O.S. D-2B	Unknown	France
OSD/LT OIL SPILL DISPERSANT	Type 1	UK
OSR 4000	Type 1	UK
RADIAGREEN OSD	Type 2/3	France, Spain, UK
SEACARE ECOSPERSE	Type 2/3	UK
SEACARE ECOSPERSE 52	Type 2/3	UK
SEACARE OSD	Type 1	UK
SHELL DISPERSANT CONCENTRATE	Type 2	Cyprus
SHELL DISPERSANT LT	Type 1	Cyprus
SUPER DISPERSANT 25	Type 2/3	Cyprus, Greece, UK
VECLEAN OIL DISPERSANT	Type 2/3	UK
UNICLEAN OSD ENVIRO	Type 2/3	Greece
W-2096	Type 2/3	UK
ZI-400 (formerly TI-400 OIL SPILL DISPERSANT)	Unknown	USA

3.2.1 Effectiveness of commercial dispersants

Empirical models of oil dispersibility with Corexit 9500—as measured in the swirling-flask laboratory test—were also recently developed (Fingas et al., 2003). These models, which range in complexity from two (viscosity and density) to fourteen parameters, were developed by determining the effects of twenty-nine physical and chemical properties on oil dispersibility. Viscosity was found to be the most important physical property in determining dispersibility, but various aspects of chemical composition (e.g., the concentrations of *n*-dodecane, *n*-hexacosane, and naphthalenes) were more highly correlated (National research Council, 2005). The most effective models were used to predict the dispersibility of 295 oils in the Environment Canada oil properties catalogue (National Research Council, 2005). Although these correlations may be useful for predicting and ranking the dispersibility of a large number of oils, the authors caution that the laboratory tests (upon which the correlations



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are based) may not provide a direct representation of what can be obtained in the field where different salinity and energy regimes are likely to be encountered.

In table 5 are reported the available data about the effectiveness of some commercial dispersants tested by the U.S. Environmental Protection Agency (EPA).

The overall effectiveness of oil dispersion has three components: (1) operational effectiveness, which describes the encounter probability of the dispersant application and the ability of the dispersant to become incorporated into the floating oil, (2) chemical effectiveness, which is measured by the fraction of treated surface oil that becomes stably entrained as small droplets in the water column, and (3) hydrodynamic effectiveness, which describes the transport of the chemically dispersed oil plume and its dilution by turbulent diffusion through horizontal and vertical mixing processes. Operational effectiveness is determined by site-specific parameters, such as the patchy distribution of oil on the water surface, the ability to accurately target and hit the thicker parts of oil slicks with the dispersant spray, and the size distribution and impact velocity of dispersant droplets that hit the floating oil. It is difficult to simulate important characteristics of dispersant application in laboratory-scale.

Table 6: Swirling flask dispersant effectiveness test with South Louisiana (S/L) and Prudhoe Bay (P/B) crude oils

Product	Type of Oil	Efficacy	Reference
BIODISPERS	Prudhoe Bay Crude	51.0%	Technical Product Bulletin #D-9 USEPA, Oil Program Center
	S. Louisiana Crude	63.0%	Original Listing Date: JUNE 28, 2002
JD-109	Prudhoe Bay Crude	26.0%	Technical Product Bulletin #D-6 USEPA, Oil Program Center
	S. Louisiana Crude	91.0%	Original Listing Date: September 20, 2000
NOKOMIS 3-AA	Prudhoe Bay Crude	63.20%	Technical Product Bulletin #D-14 USEPA, Oil Program Center
	S. Louisiana Crude	65.70%	Original Listing Date: July 31, 2008
JD-2000	Prudhoe Bay Crude	60.4%	Technical Product Bulletin #D-7 USEPA, Oil Program Center
	S. Louisiana Crude	77.8%	Original Listing Date: August 6, 2001
NOKOMIS 3-F4	Prudhoe Bay Crude	62.20%	Technical Product Bulletin #D-8 USEPA, Oil Program Center
	S. Louisiana Crude	64.90%	Original Listing Date: March 4, 2002
COREXIT 9527	Prudhoe Bay Crude	37.40%	Technical Product Bulletin #D-1 USEPA, Oil Program Center
	S. Louisiana Crude	63.40%	Original Listing Date: March 10, 1978 Revised Listing Date: December 18, 1995
MARE CLEAN 200	Prudhoe Bay Crude	63.97%	Technical Product Bulletin #D-3 USEPA, Oil Program Center
	S. Louisiana Crude	84.14%	Original Listing Date: February 23, 1988 Revised Listing Date: January 26, 1996

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SAF-RON GOLD	Prudhoe Bay Crude	84.80%	Technical Product Bulletin #D-12 USEPA, Oil Program Center Original Listing Date: January 3, 2005
	S. Louisiana Crude	53.80%	
DISPERSIT SPC1000	Prudhoe Bay Crude	40.00%	Technical Product Bulletin #D-2 USEPA, Oil Program Center Original Listing Date: April 22, 1985 Revised Listing Date: January 26, 1996
	S. Louisiana Crude	105.00%	
NEOS AB-3000	Prudhoe Bay Crude	19.70%	Technical Product Bulletin #D-2 USEPA, Oil Program Center Original Listing Date: April 22, 1985 Revised Listing Date: January 26, 1996
	S. Louisiana Crude	89.80%	
SEA BRAT 4	Prudhoe Bay Crude	53.55%	Technical Product Bulletin #D-10 USEPA, Oil Program Center Original Listing Date: November 26, 2002
	S. Louisiana Crude	60.65%	

3.2.2 Toxicity of commercial dispersants

A standard toxicity test is to measure the acute lethal toxicity to standard species. The LC₅₀ of a substance is the 'Lethal Concentration to 50% of a test population', usually given in mg/L, which is approximately equivalent to parts per million. The specification is also given with a time period, which is often 96 hours for larger test organisms such as fish. Lower LC values correspond to higher toxicities. The toxicity of dispersants themselves as used in the early 1970s ranged from about 5 to 50 mg/L measured as an LC to the 50 % of the specimens in a standard time period (often 48-96 hours). Dispersants available today usually vary in a wide range, few up to 500 mg/L (LC₅₀) in toxicity and contain a mixture of surfactants and a less toxic solvent (Laurier, 2000). In Table 6 are indicated the toxicity of some commercial dispersants as reported by U.S. Environmental Protection Agency. Table 7 provides some additional data from literature about some of the more diffused commercial dispersants.

Table 7: Toxicity of commercial dispersants as reported from U.S. Environmental Protection Agency

PRODUCT	Target species	LC ₅₀ mg/L (ending point)
BIODISPERS	<i>Menidia beryllina</i>	13.46 (96-hr)
	<i>Mysidopsis bahia</i>	78.90 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	12.42 (96-hr)
	<i>Mysidopsis bahia</i>	2.82 (48-hr)
BIODISPERS & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	5.95 (96-hr)
	<i>Mysidopsis bahia</i>	2.66 (48-hr)
Reference Toxicant (SDS)	<i>Menidia beryllina</i>	11.84 (96-hr)
	<i>Mysidopsis bahia</i>	21.81 (48-hr)
COREXIT® EC9500A	<i>Menidia beryllina</i>	25.20 (96-hr)
	<i>Mysidopsis bahia</i>	32.23 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	10.72 (96-hr)
	<i>Mysidopsis bahia</i>	16.12 (48-hr)
COREXIT® EC9500A & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	2.61 (96-hr)
	<i>Mysidopsis bahia</i>	3.40 (48-hr)
Reference Toxicant (SDS)	<i>Menidia beryllina</i>	7.07 (96-hr)
	<i>Mysidopsis bahia</i>	9.82 (48-hr)



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COREXIT® EC9527A	<i>Menidia beryllina</i>	14.57 (96-hr)
	<i>Mysidopsis bahia</i>	24.14 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	10.72 (96-hr)
	<i>Mysidopsis bahia</i>	16.12 (48-hr)
COREXIT® EC9527A & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	4.49 (96-hr)
	<i>Mysidopsis bahia</i>	6.60 (48-hr)
Reference Toxicant (DSS)	<i>Menidia beryllina</i>	7.07 (96-hr)
	<i>Mysidopsis bahia</i>	9.82 (48-hr)
DISPERSIT SPC 1000™	<i>Menidia beryllina</i>	3.5 (96-hr)
	<i>Mysidopsis bahia</i>	16.6 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	11.6 (96-hr)
	<i>Mysidopsis bahia</i>	11.7 (48-hr)
DISPERSIT SPC 1000™ & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	7.9 (96-hr)
	<i>Mysidopsis bahia</i>	8.2 (48-hr)
Reference Toxicant (SDS)	<i>Menidia beryllina</i>	6.3 (96-hr)
	<i>Mysidopsis bahia</i>	11.7 (48-hr)
JD-109	<i>Menidia beryllina</i>	1.90 (96-hr)
	<i>Mysidopsis bahia</i>	1.18 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	9.35 (96-hr)
	<i>Mysidopsis bahia</i>	3.13 (48-hr)
JD-109 & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	3.84 (96-hr)
	<i>Mysidopsis bahia</i>	3.51 (48-hr)
Reference Toxicant (DSS)	<i>Menidia beryllina</i>	2.63 (96-hr)
	<i>Mysidopsis bahia</i>	8.06 (48-hr)
JD-2000™	<i>Menidia beryllina</i>	407.00 (96-hr)
	<i>Mysidopsis bahia</i>	90.50 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	8.39 (96-hr)
	<i>Mysidopsis bahia</i>	2.58 (48-hr)
JD-2000™ & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	3.59 (96-hr)
	<i>Mysidopsis bahia</i>	2.19 (48-hr)
Reference Toxicant (SDS)	<i>Menidia beryllina</i>	2.22 (96-hr)
	<i>Mysidopsis bahia</i>	10.50 (48-hr)
MARE CLEAN 200	<i>Menidia beryllina</i>	1996 (96-hr)
	<i>Mysidopsis bahia</i>	938 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	10.72 (96-hr)
	<i>Mysidopsis bahia</i>	16.12 (48-hr)
MARE CLEAN 200 & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	42 (96-hr)
	<i>Mysidopsis bahia</i>	9.84 (48-hr)
Reference Toxicant (SDS)	<i>Menidia beryllina</i>	7.07 (96-hr)
	<i>Mysidopsis bahia</i>	9.82 (48-hr)
NEOS AB3000	<i>Menidia beryllina</i>	91.1 (96-hr)
	<i>Mysidopsis bahia</i>	33.0 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	201.8 (96-hr)
	<i>Mysidopsis bahia</i>	11.5 (48-hr)
NEOS AB3000 & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	57. (96-hr)
	<i>Mysidopsis bahia</i>	25.0 (48-hr)
Reference Toxicant (DSS)	<i>Menidia beryllina</i>	1.5 (96-hr)
	<i>Mysidopsis bahia</i>	9.3 (48-hr)
NEOS AB3000	<i>Menidia beryllina</i>	91.1 (96-hr)
	<i>Mysidopsis bahia</i>	33.0 (48-hr)



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NOKOMIS 3-AA	<i>Menidia beryllina</i>	34.22 (96-hr)
	<i>Mysidopsis bahia</i>	20.16 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	22.50 (96-hr)
	<i>Mysidopsis bahia</i>	11.07 (48-hr)
NOKOMIS 3-AA & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	7.03 (96-hr)
	<i>Mysidopsis bahia</i>	5.56 (48-hr)
Reference Toxicant (CuSO ₄)	<i>Menidia beryllina</i>	5.36 (96-hr)
	<i>Mysidopsis bahia</i>	7.83 (48-hr)
NOKOMIS 3-F4	<i>Menidia beryllina</i>	29.80 (96-hr)
	<i>Mysidopsis bahia</i>	32.20 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	100.00 (96-hr)
	<i>Mysidopsis bahia</i>	72.70 (48-hr)
NOKOMIS 3-F4 & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	100.00 (96-hr)
	<i>Mysidopsis bahia</i>	58.40 (48-hr)
Reference Toxicant (DSS)	<i>Menidia beryllina</i>	159.6 (96-h)
	<i>Mysidopsis bahia</i>	
SAF-RON GOLD	<i>Menidia beryllina</i>	29.43 (96-hr)
	<i>Mysidopsis bahia</i>	63.00 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	16.76 (96-hr)
	<i>Mysidopsis bahia</i>	5.93 (48-hr)
SAF-RON GOLD & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	9.25 (96-hr)
	<i>Mysidopsis bahia</i>	3.04 (48-hr)
Reference Toxicant (SLS)	<i>Menidia beryllina</i>	15.94 (96-hr)
	<i>Mysidopsis bahia</i>	9.83 (48-hr)
SEA BRAT #4	<i>Menidia beryllina</i>	30.00 (96-hr)
	<i>Mysidopsis bahia</i>	14.00 (48-hr)
No. 2 Fuel Oil	<i>Menidia beryllina</i>	16.00 (96-hr)
	<i>Mysidopsis bahia</i>	14.00 (48-hr)
SEA BRAT #4 & No. 2 Fuel Oil (1:10)	<i>Menidia beryllina</i>	23.00 (96-hr)
	<i>Mysidopsis bahia</i>	18.00 (48-hr)
Reference Toxicant (DSS)	<i>Menidia beryllina</i>	1.14 (96-hr)
	<i>Mysidopsis bahia</i>	0.98 (48-hr)



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Table 8: Additional data on toxicity of commercial dispersants

PRODUCT	Target species	LC ₅₀ – EC50 (ppm)	Reference
NOKOMIS 3	<i>Athennops affinis</i>	482 - 729	Singer et al. 1994
	<i>Macrocystis pyrifera</i>	730 – 794	
Slick A Way	<i>Athennops affinis</i>	437 - 458	
	<i>Macrocystis pyrifera</i>	730 - 959	
COREXIT 9500	<i>Americanensis bahia</i>	32	Fuller et al. 2004
	<i>Menidia beryllina</i>	79	
	<i>Cyprinodon variegatus</i>	180	
	<i>Vibrio fischeri</i>	170 (15 min EC50)	
COREXIT 9500	<i>Americanensis bahia</i>	21	Edward et al., 2003
	<i>Menidia beryllina</i>	79	
COREXIT 9500	<i>Hydra viridissima</i>	160	Mitchell and Holdaway (2000)
	<i>Hydra viridissima</i>	13	Mitchell and Holdaway (2000)
	<i>Allorchestes compressa</i>	3.5	Gulec et al. (1997)
	<i>Artemia salina</i>	21	George-Ares and Clark (2000)
	<i>Palaemonetes varians</i>	8103	Beupoil and Nedelec (1994)
	<i>Palaemon serenus</i>	83.1	Gulec and Holdaway (2000)
	<i>Mysidopsis bahia</i>	32.2	Inchcape Testing Services (1995)
	<i>Mysidopsis bahia</i>	31.4-35.9	George-Ares and Clark (2000); Fuller and Bonner (2001); Clark et al.(2001); Rhoton et al. (2001)
	<i>Mysidopsis bahia</i>	500-1305 >789	Coehlo and Aurand (1997); Fuller and Bonner (2001); Clark et al. 2001); Rhoton et al. (2001)
	<i>Eurytemora affinis</i>	5.2	Wright and Coehlo (1996)
	<i>Holmesimys costata</i>	158-245	Singer et al. (1996)
	<i>Holmesimys costata</i>	41.4-142	Singer et al. (1996)
	<i>Penaeus monodon</i>	48	Marine and Freshwater Resources Institute (1998)
	<i>Chionoecetes bairdi</i>	5.6	Rhoton et al. (2001)
	<i>Chionoecetes bairdi</i>	355	Rhoton et al. (2001)
	<i>Polinices conicus</i>	42.3	Gulec et al. (1997)
	<i>Haliotis rufescens</i>	0.7	Aquatic Testing Laboratories (1994)
	<i>Haliotis rufescens</i>	5.7-9.7	Singer et al. (1996)
	<i>Haliotis rufescens</i>	12.8-19.7	Singer et al. (1996)



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	<i>Lates carcarifer</i>	143	Marine and Freshwater Resources Institute (1998)
	<i>Scophtalmus maximus</i>	74.7	George-Ares & Clark (2000); Clark et al. (2001)
	<i>Scophtalmus maximus</i>	>1055	George-Ares & Clark (2000); Clark et al. (2001)
	<i>Oncohynchus mykiss</i>	354	George-Ares and Clark (2000)
	<i>Fundulus heteroclitus</i>	140	George-Ares and Clark (2000)
	<i>Cyprinodon variegatus</i>	170-193	Fuller and Bonner (2001)
	<i>Cyprinodon variegatus</i>	593-750	Fuller and Bonner (2001)
	<i>Sarotherodon mozambicus</i>	150	George-Ares and Clark (2000)
	<i>Brachydanio rerio</i>	>400	George-Ares and Clark (2000)
	<i>Menidia beryllina</i>	25.2-85.4	Inchcape Testing Services (1995); Fuller and Bonner (2001); Rhoton et al., 2001
	<i>Menidia beryllina</i>	40.7-116.6, 205	Fuller and Bonner (2001); Rhoton et al. (2001)
COREXIT 9527	<i>Hydra viridissima</i>	230	Mitchell & Holdaway (2000)
	<i>Hydra viridissima</i>	<15 (NOEC)	Mitchell & Holdaway (2000)
	<i>Artemia sp.</i>	52-104	Wells et al. (1982)
	<i>Artemia salina</i>	53-84	Briceno et al. (1992)
	<i>Gnoringospaeroma oregonensis</i>	>1000	Duval et al. (1982)
	<i>Anonyx laticoxae</i>	>140	Foy (1982)
	<i>Anonyx nugax</i>	97-111	Foy (1982)
	<i>Boeckosimus sp.</i>	>175 Foy	Foy (1982)
	<i>Boeckosimus edwardsi</i>	>80	Foy (1982)
	<i>Onisimus litoralis</i>	80-160	Foy (1982)
	<i>Gammarus oceanicus</i>	>80	Foy (1982)
	<i>Allorchestes compressa</i>	3.0	Gulec et al. (1997)
	<i>Pseudocalanus minutus</i>	8-12	Wells et al. (1982)
	<i>Pseudocalanus minutus</i>	5-25	Wells et al. (1982)
	<i>Palaemonetes pugio</i>	640 (27°C)	National Research Council (1989)
	<i>Palaemonetes pugio</i>	840 (17°C)	National Research Council (1989)
	<i>Palaemon serenus</i>	49.4	Gulec and Holdaway (2000)
	<i>Macrobrachium rosenbergii</i>	80.4	Law (1995)
	<i>Penaeus monodon</i>	35-45	Fucik et al. (1995)
	<i>Penaeus vannemai</i>	35-45	Fucik et al. (1995)
	<i>Penaeus setiferus</i>	11.9	Fucik et al. (1995)
	<i>Mysidopsis bahia</i>	29.2, 19-34	Briceno et al. (1992); George-Ares et al. (1999); Exxon Biom. Sci. (1993); Pace & Clark (1993)
	<i>Mysidopsis bahia</i>	24.1-29.2	Inchcape Testing Services (1995); Clark et al. 2001



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<i>Mysidopsis bahia</i>	>1014	Pace et al. (1995); Clark et al. (2001)
<i>Holmesimysis costata</i>	2.4–10.1	Pace and Clark (1993); Exxon Biomedical Sciences (1993); Clark et al. 2001
<i>Holmesimysis costata</i>	195	George-Ares and Clark (2000); Clark et al. (2001)
<i>Holmesimysis costata</i>	4.3–7.3	Singer et al. (1990, 1991)
<i>Holmesimysis costata</i>	120–163	Singer et al. (1991)
<i>Holmesimysis costata</i>	15.3	Coelho and Aurand (1996); Fucik et al. (1995)
<i>Callinectes sapidus</i>	77.9–81.2	Ordsie and Garofalo (1981)
<i>Argopecten irradians</i>	200 (20°C)	Ordsie and Garofalo (1981)
<i>Argopecten irradians</i>	1800 (10°C)	Ordsie and Garofalo (1981)
<i>Argopecten irradians</i>	2500 (2°C)	Singer et al. (1990, 1991)
<i>Haliotis rufescens</i>	1.6–2.2d	Singer et al. (1991)
<i>Haliotis rufescens</i>	13.6–18.1	Hartwick et al. (1982)
<i>Protothaca stamiea</i>	ca. 100	George-Ares and Clark (2000); Clark et al. (2001)
<i>Crassostrea gigas</i>	3.1d	George-Ares and Clark (2000); Clark et al. (2001)
<i>Crassostrea gigas</i>	13.9	Gulec et al. (1997)
<i>Polinices conicus</i>	33.8	George-Ares and Clark (2000)
<i>Oryzias latipes</i>	130–150 -400	Wells and Doe (1976)
<i>Oncorhynchus mykiss</i>	96–293	Slade (1982)
<i>Leiostomus xanthurus</i>	61.2–62.3	Fucik et al. (1995)
<i>Leiostomus xanthurus</i>	27.4	Singer et al (1990, 1991)
<i>Atherinops affinis</i> (larvae)	25.5–40.6	Singer et al. (1991)
<i>Atherinops affinis</i> (larvae)	59.2–104d	Foy (1982)
<i>Myoxocephalus quadricornis</i>	<40	Briceno et al. (1992)
<i>Fundulus heteroclitus</i>	99–124	Briceno et al. (1992); Fucik et al. (1995); Pace and Clark (1993); Inchcape Testing Services (1995);
<i>Menidia beryllina</i> (larvae)	52.3, 14.6–57	Exxon Biomedical Sciences (1993); Clark et al. (2001)
<i>Menidia beryllina</i> (larvae)	58.3	George-Ares and Clark (2000); Clark et al.(2001)
<i>Menidia beryllina</i> (larvae)	>100	Fucik et al. (1995)
<i>Sciaenops ocellatus</i> (embryo-larval)	52.6	Fucik et al. (1995)
<i>Cyprinodon variegatus</i>	74–152	Briceno et al. (1992)
<i>Brevoortia tyrannus</i> (embryo-larval)	42.4	Fucik et al. (1995)
<i>Macquaria novemaculeata</i> (larvae)	14.3	Gulec and Holdaway (2000)
<i>Thalassia tesudimum</i>	200	Baca and Getter (1984)
<i>Macrocystis pyrifera</i> (zoospores)	1.3–2.1 (NOEC)	Singer et al. (1990, 1991)
<i>Macrocystis pyrifera</i> (zoospores)	12.2–16.4 (NOEC)	Singer et al. (1991)



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<i>Macrocystis pyrifera</i> (zoospores)	86.6d–102	Singer et al. (1991)
<i>Phyllospora comosa</i>	30	Burridge and Shir (1995)
<i>Vibrio fisheri</i>	4.9–12.8	George-Ares et al. (1999); Exxon Biomedical Sciences (1992)



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