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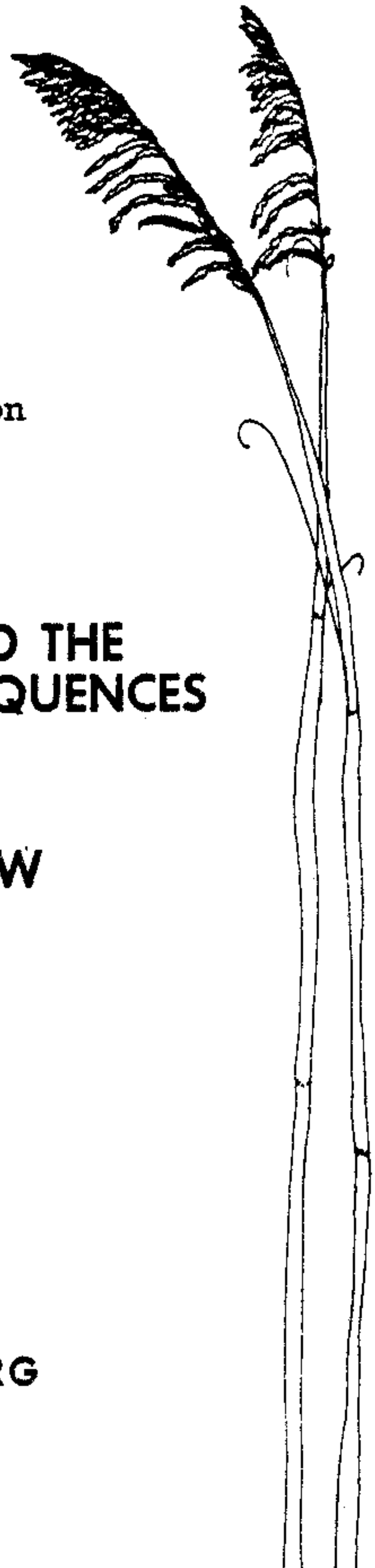

State of Florida
Department of
Environmental Regulation

OIL DISPERSANTS AND THE ENVIRONMENTAL CONSEQUENCES OF THEIR USAGE:

A LITERATURE REVIEW

CRAIG W. DYE
RUSSEL B. FRYDENBORG

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OIL DISPERSANTS AND THE ENVIRONMENTAL CONSEQUENCES OF THEIR USAGE: A LITERATURE REVIEW

By

Craig W. Dye

Russel B. Frydenborg

Department of Environmental Regulation

Tallahassee, Florida

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INTRODUCTION

The State of Florida, with over 27,000 sq. miles of coastline (Jones 1974) is particularly vulnerable to the devastations of a massive oil spill similar to the Amoco Cadiz disaster. This is especially true since Florida is also located astride several major shipping lanes that connect Middle Eastern oil supplies and Gulf Coast refineries. Barge traffic carrying refined petroleum products on the extensive Intracoastal Waterway system in Florida may also be a source of chronic and/or catastrophic oil pollution. Additionally, oil drilling activities on the continental shelf in the Gulf of Mexico pose potential threats since blowouts are liable to occur at any time (e.g. the Campeche blow-out). Indeed the Gulf of Mexico, during the period 1973-77, suffered the largest number of oil pollution incidents of all the coastal and inland waters in the United States (Fugaro and Boyd 1978).

It seems obvious then, that Florida should be prepared to deal with oil spills in terms of spill prevention and clean-up techniques. Since this agency (DER) is primarily concerned with minimizing the ecological damage of spilled oil, this paper will review the literature pertaining to a particular control technique, the use of oil dispersants.

Oil spills in the aquatic environment present a short term hazard to the biota of the affected area as well as to human health and welfare (Ruel et al. 1973; Biglane 1977). Oil spills may also present a threat of long term damage to aquatic life in the vicinity of a spill (Blumer and Sass 1972; Vandermeulen and Gordon 1976). Therefore, while it is obviously desirable to physically remove spilled oil from the environment (Cowell 1978), in some instances chemical dispersal of the oil may be the only practical alternative (Ruel et al. 1973).

Dispersants are chemicals that, with sufficient mixing, aid the dispersion of oil in water, (i.e., by increasing surface area of the oil through the creation of small droplets)(Canevari 1969). Ruel et al. (1973) list a number of advantages and disadvantages to using oil dispersants:

Advantages:

1. The rate of oil biodegradation is increased because of the increased surface-to-volume ratio;

2. damage to waterfowl is decreased since oil is removed from the water surface;

3. fire hazards may be reduced;

4. adherance of oil to most surfaces is reduced; and

5. the formation of tar-like residue is prevented.

Disadvantages:

1. Most dispersants have toxic effects on aquatic organisms;

2. the increased surface-to-volume ratio increases the toxicity of the oil to aquatic organisms;

3. the dispersed oil is difficult to remove from surface water supplies;

4. because many dispersants are unable to effectively disperse floating oil, the above advantages cannot be realized;

5. the fate of oil once it has been dispersed is not well known; and

6. application of dispersant on volatile oils may increase fire hazards.

Although the use of dispersants may be desirable in certain circumstances, the known toxicity of dispersants and the general lack of knowledge about the fate of dispersed oil in an aquatic environment require that guidelines for their use be developed. It is the objective of this paper to evaluate all available current scientific literature and then present a technical basis for developing such guidelines.

PETROLEUM IN AQUATIC ECOSYSTEMS

Physical-Chemical Properties of Oils

Crude oils and refined petroleum exhibit a tremendous complexity of, and variation in, chemical makeup. Since clean-up techniques, including the use of chemical agents, are dependent on the composition of a particular oil, a knowledge of the major components and their properties is essential (Wilson 1978; Thornton 1979).

Using gross compositional data on all world crudes, the following approximate composition may be determined for the "average" crude oil:

By molecular size (carbon chain length) - gasoline (C_5-C_{10}), 30%; kerosene (C_{10}-C_{12}), 10%; light distillate oil (C_{12}-C_{20}), 15%; heavy distillate oil (C_{20}-C_{40}), 25%; residuum oil ($>C_{40}$), 20%.

By molecular type - paraffin hydrocarbons (alkanes), 30%; napthene hydrocarbons (cycloalkanes), 50%; aromatic hydrocarbons, 15%; nitrogen, sulphur, and oxygen containing compounds (NSO's), 5% (Wilson 1975).

However, crude oils from different geologic and geographic sources vary widely in chemical composition, viscosity, solubility, boiling point, pour point, mineral content, and relative abundance of the afore-mentioned molecular components (Smith, H. 1968). The following table (Table 1) illustrates the disparities between four oils with regard to their solubilities, specific water soluble fraction hydrocarbon contents, and hydrocarbon composition of mechanically induced oil-in-water dispersions.

Sources and Fates of Oil in the Marine Environment

Wilson (1975) has estimated the input of petroleum hydrocarbons considered significant to the world oceans (Table 2).

Wilson calculated that by the early 1980's the total input, particularly from transportation accidents and operations, should be significantly reduced due to more stringent operating regulations. Nevertheless transportation accidents and operations constitute a significant portion of the petroleum input budget and are frequently the cause of catastrophic point source oil pollution. There are a number of natural physical and chemical factors that aid the dispersion and ultimate degradation of petroleum hydrocarbons in an

Table 1. Specific hydrocarbon content (ppm) of water-soluble fraction from 10% oil-in-water solution of the 4 test oils (after Anderson *et al.*, 1974).

Compound	South Louisiana crude oil	Kuwait crude oil	No. 2 fuel oil	Bunker C residual oil
Alkanes				
Ethane	0.54	0.23	a	a
Propane	3.01	3.30		
Butane	2.36	3.66		
Isobutane	1.69	0.90	0.39	0.05
Pentane	0.49	1.31		
Isopentane	0.70	0.98		
Cyclopentane + 2-methylpentane	0.38	0.59	0.02	0.005
Methylcyclopentane	0.23	0.19	0.019	0.004
Hexane	0.09	0.29	0.014	0.004
Methylcyclohexane	0.22	0.08	0.03	0.002
Heptane	0.06	0.09	0.02	0.004
C_{16} n-paraffin	0.012	0.0006	0.008	0.0012
C_{17} n-paraffin	0.009	0.0008	0.006	0.0019
Total C_{12}-C_{24} n-paraffins	0.089	0.004	0.047	0.012
Aromatics				
Benzene	6.75	3.36	0.55	0.04
Toluene	4.13	3.62	1.04	0.08
Ethylbenzene + m-, p-xylenes	1.56	1.58	0.95	0.09
o-xylene	0.40	0.67	0.32	0.03
Trimethylbenzenes	0.76	0.73	0.97	0.11
Naphthalene	0.12	0.02	0.84	0.21
1-Methylnaphthalene	0.06	0.02	0.34	0.19
2-Methylnaphthalene	0.05	0.008	0.48	0.20
Dimethylnaphthalenes	0.06	0.02	0.24	0.20
Trimethylnaphthalenes	0.008	0.003	0.03	0.10
Biphenyl	0.001	0.001	0.011	0.001
Methylbiphenyls	0.001	0.001	0.014	0.001
Dimethylbiphenyls	0.001	0.001	0.003	0.001
Fluorene	0.001	0.001	0.009	0.005
Methylfluorenes	0.001	0.001	0.009	0.004
Dimethylfluorenes	0.001	0.001	0.002	0.002
Dibenzothiophene	0.001	0.001	0.004	0.001
Phenanthrene	0.001	0.001	0.010	0.009
Methylphenanthrenes	0.002	0.001	0.007	0.011
Dimethylphenanthrenes	0.001	0.001	0.003	0.003
Total saturates	9.86	11.62	0.54	0.081
Total aromatics	13.90	10.03	5.74	1.28
Total dissolved hydrocarbons measured	23.76	21.65	5.28	1.36

[a]Unresolved gas-chromatography peaks, probably include some olefins

Table 2. Budget of Petroleum Hydrocarbons Introduced into the Oceans (after Wilson, 1975)

Source	Input Rate (mta)[a]		Reference
	Best Estimate	Probable Range	
Natural seeps	0.6	0.2-1.0	Wilson *et al.* (1973)
Offshore production	0.08	0.08-0.15	Wilson *et al.* (1973)
Transportation			
LOT tankers	0.31	0.15-0.4	Results of workshop panel deliberations
Non-LOT tankers	0.77	0.65-1.0	
Dry docking	0.25	0.2-0.3	
Terminal operations	0.003	0.0015-0.005	
Bilges bunkering	0.5	0.4-0.7	
Tanker accidents	0.2	0.12-0.25	
Nontanker accidents	0.1	0.02-0.15	
Coastal refineries	0.2	0.2-0.3	Brummage (1973a)
Atmosphere	0.6	0.4-0.8	Feuerstein (1973)
Coastal municipal wastes	0.3	-	Storrs (1973)
Coastal, Nonrefining, industrial wastes	0.3	-	Storrs (1973)
Urban runoff	0.3	0.1-0.5	Storrs (1973), Hallhagen (1973)
River runoff	1.6	-	Storrs (1973), Hallhagen (1973)
TOTAL	6.113		

[a] mta, million metric tons.

aquatic system (Blumer et al. 1973; Ministry of Defense 1973, Wilson 1975; Gordon et al. 1976; Gundlach et al. 1978). Burwood and Speers (1974) have diagrammed these processes (Figure 1).

The basic physical-chemical processes include: 1) initial spreading of the oil slick by gravity; the rate being controlled by interfacial and viscous drag forces; 2) evaporation of the volatile hydrocarbon fractions, generally low molecular weight aromatics and other hydrocarbons with low boiling points (Brown and Huffman 1976) (evaporation is also a principal process affecting residues on the sea surface (Butler 1975, 1976)); 3) solution and dissolution of the low boiling point, low molecular weight and polar hydrocarbons (Guard et al. 1975); 4) emulsification of the heavier fractions of crude oil into a persistent water-in-oil emulsion called "chocolate mousse"; 5) direct sea-air exchange via wave produced spray and bursting bubbles (Harrison et al. 1975); 6) photochemical oxidation of thin films of oil by breaking down long-chain hydrocarbon molecules and, with the addition of oxygen, creating more soluble and/or volatile compounds (Young and Sethi 1975); 7) tar lump formation of long chain paraffinic hydrocarbons (up to C_{40}); and finally 8) sedimentation of agglutinated particles following absorption or adsorption onto particulate matter, including phytoplankton (Lee and Anderson 1977).

In addition to the physical and chemical weathering processes discussed previously, biological degradation of the oil (primarily microbial) proceeds concurrently and is responsible for ultimately mineralizing the non-volatile hydrocarbon fractions (Atlas and Bartha 1972b; Atlas 1975; Wilson 1975; Lee and Anderson 1977).

A number of bacterial and fungal species capable of metabolizing various hydrocarbon fractions have been isolated. Davies and Hughes (1968) found that *Corynebacterium* sp., *Nocardia* sp., *Streptomyces* sp., *Penicillium* sp., *Candida* sp., *Mycobacterium* sp., *Micrococcus* sp. and *Pseudomonas* sp. could metabolize alkanes, cycloalkanes and aromatics. Atlas and Bartha (1972a) isolated strains of *Flavobacterium* sp. and *Brevibacterium* sp. that metabolized paraffinic crude oil as well as a model hydrocarbon mixture. Additionally, Zajic and Supplisson (1972) showed that metabolic products of certain bacteria possess properties of surfactants and that these particular organisms would also selectively metabolize n-paraffins.

Although microbial degradation of oil is a significant process in the ultimate fate of oil at sea, the rate of degradation is highly variable and depends on a number of environmental conditions (Ministry of Defense 1973; Wilson 1975). The two most important factors that have been noted to control the rate of biodegradation of oil are temperature and nutrient concentration (Hughes 1968; Atlas and Bartha 1973; Blumer et al. 1973; Mulkin-Phillips and Stewart 1974; Walker et al. 1975). Atlas (1975) and Jobson et al. (1972) found that microbial degradation of oil proceeded at a much faster rate at 20°C than at 4°C. Gibbs et al. (1975) also noted increased biodegradation of oil at 14°C compared with oil at 4°C.

Nutrient additions (primarily nitrogen and phosphorus compounds) have been shown to increase biodegradation of oil (Tagger *et al.* 1976). Atlas and Bartha (1972b) determined that biodegradation of an oil mixture, with NO_3 and PO_4 added, increased 70% compared with untreated oil mixture. Olivieri *et al.* (1976) also noted similar increases in biodegradation using a lipophilic fertilizer ($MgNH_4PO_4$).

Physical agitation and aeration, in a laboratory environment, also proved helpful in stimulating biodegradation (Soli and Bens 1972; Davis and Gibbs 1975). Similarly, Rashid (1974) noted that microbial degradation of oil proceeded at a greater rate in a high energy beach area than in low energy bays. In any case, rates of degradation were found to vary from a matter of weeks (Atlas and Bartha 1972a; Lee and Anderson 1977) to years (Blumer *et al.* 1973; Rashid 1974).

Effects of Oil in the Marine Environment

The ecological impact of oil spills, particularly the immediate effects, have been the subject of numerous investigations (*e.g.* McAuliffe *et al.* 1975; Bates 1978). The growth of bacterial populations studied by Walker *et al.* (1974) was inhibited by the presence of #2 fuel oil and South Louisiana crude. Hodson *et al.* (1977) also noted inhibition of D-glucose mineralization by heterotrophic populations in low concentrations of several types of crude and fuel oils. Marine phytoplankton activity was found to be significantly inhibited by 300 μg/l.

Toxicity and inhibition of photosynthesis has also been observed in marine algae (Gordon and Prouse 1973; Lacaze 1974) and freshwater phytoplankton (Federle *et al.* 1979). Toxicity of #2 fuel oil to sensitive marine diatoms has been noted at concentrations between 40-400 ppb (Pulich *et al.* 1974). Winters *et al.* (1977) isolated phenalen-1-one (a water soluble compound in #2 fuel oil) and found it to be toxic, under certain light conditions, to two species of green algae at 250 ppb and to a blue-green species at 5 ppm. Inhibition of photosynthesis in certain marine microalgae has been noted at dose levels of the water soluble fractions of crude and refined oils as low as 1 - 45 ug/mg dry weight of algal cells (Armstrong and Calder 1978). Additionally, carcinogenic effects have been observed in the marine seaweed *Porphyra* grown in muds with high concentrations of aromatic hydrocarbons (Boney 1974). However, several authors (Parsons *et al.* 1976; Prouse *et al.* 1976) have noted growth stimulation in algal populations subjected to low concentrations (in ppb range) of mineral hydrocarbons. It is difficult to extrapolate the results of these controlled tests to the environment since organism response is variable and the oil concentration and composition changes during the course of an oil spill (Prouse *et al.* 1976).

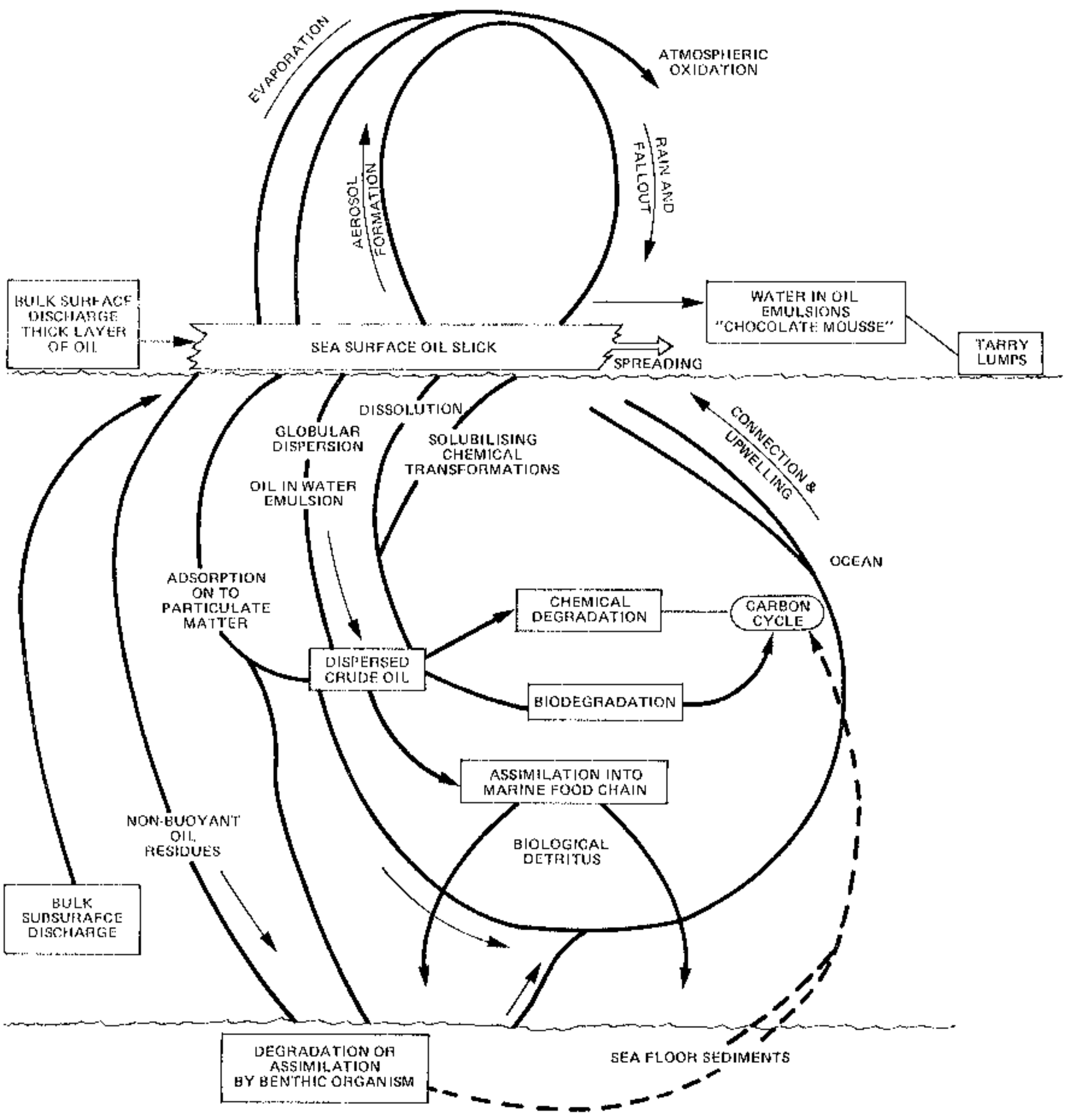

Figure I. Processes involved in the fate of spilled crude oil in the marine environment. (After Burwood and Speers, 1974)

Studies of petroleum effects on zooplankton (primarily copepods) have indicated sublethal consequences such as significant reductions in life span, total number of eggs produced, mean brood size and rate of reproduction (Berdugo et al. 1977). Additionally, zooplankton species are known to concentrate large amounts of hydrocarbons in their tissues even though they were exposed to very low concentrations (0.10 - 50 ug/l) of petroleum (Corner et al. 1976; Berdugo et al. 1977; Mackie et al. 1978).

Petroleum effects on other invertebrates are quite variable; their severity being basically a function of exposure time and concentration (Stegeman and Teal 1973; Lee et al. 1977). Grant (1970) found that *Favia speciosa*, a coral, could survive short term exposures (several days) to oil floating on the surface above a reef. Additionally, Bak and Elgershuizen (1976) in their work with coral, determined that the water soluble fraction of crude oil was the primary cause of toxicity rather than actual physical contact with oil-sediment particles. Allen's (1971) tests with developing embryos of the sea urchin *Strongylocentrotus purpuratus* indicated that the various crude and refined oils tested were highly toxic to the developing eggs but did not inhibit fertilization. Investigations of the effects of crude and fuel oils on the soft shell clam, *Mya arenaria*, have shown that growth rates were depressed (Gilfillan et al. 1976), that significant increases in respiration rates occurred (Fong 1976), that increased mucus secretion and clogging of gills was effected (Stainken 1976a), and that oil was concentrated in the lipid tissues (Zitko 1971; Fong 1976). Similar concentrating effects were noted by Farrington and Quinn (1973) in the clam *Mercenaria mercenaria*. Studies on hydrocarbon uptake by mussels have indicated that they can concentrate certain petroleum products more than 1000 times the ambient concentration (Fossato and Canzonier 1976), but that they are much less efficient at releasing these compounds from their tissues when replaced in clean water (Ehrhardt and Heinemann 1975; Dunn and Stich 1976). Similar results were determined for the oyster, *Crassotrea virginica* (Stegeman and Teal 1973). Tests of aqueous extracts of #2 fuel and a crude oil on the amphipods *Gammarus mucronatus* and *Amphithoe valida* showed toxicity at 0.8 ppm (fuel) and 2.4 ppm (crude) that increased with concentration and length of exposure (Lee et al. 1977).

The persistence of an oil spill will obviously determine the long term effects on the local flora and fauna. Gundlach et al. (1978) have listed wind stress, water currents, beach activity and sand grain size, tidal stage, wave energy, and oil quantity and composition as the factors important in determining the persistence of an oil spill once it has come ashore. Numerous studies have shown that once an oil spill reaches a shoreline, traces of it will remain for years in beach sediments, embayments and marshes (Young and Sethi 1975; Vandermeulen and Gordon 1976; Krebs and Burns 1977). Even though the concentration of oil is reduced due to weathering processes, herbivorous and browsing animals still concentrate oil in their tissues (Blumer et al. 1970) and there is evidence that some omnivorous and carnivorous species are able to assimilate and partially metabolize petroleum products (Scarratt and Zitko 1972).

Sub-acute effects of petroleum on shellfish consist of glycogen depletion, generalized leucocytosis of blood sinuses and increased vacuolization of the stomach and intestines (Stainken 1976b). The potential for long term damage also exists since ingested oil is only slowly metabolized by shellfish (Anderson 1972).

In higher invertebrates, such as crabs, the chronic effects of oil spills cause the disruption of pheromone chemoreception, thus altering feeding and sexual behaviour (Crapp 1971d; Guard _et al_. 1975; Krebs and Burns 1977). The ultimate results of these behavioral modifications will be to expose the affected populations to more environmental stress such as increased predation, and thus eliminate them from the oiled areas (Kittredge _et al_. 1974; Guard _et al_. 1975).

Results of sub-lethal toxicity tests using low concentrations of the water soluble fractions of crude and fuel oils on several species of estuarine fish (_Fundulus heteroclitus_ and _F. grandis_) indicate that subtle biochemical changes occur resulting in pathological damage to the structures of various cells (Ernst _et al_. 1977; Sabo and Stegeman 1977). Additionaly, Mazmanidi and Bazhashvili (1975) found that low concentrations of dissolved petroleum (0.025 to 2.500 mg/l) reduced survival rates and increased caridac frequency and a number of cell anomalies in flounder eggs and prolarvae.

Baker's (1971d, 1973) work on salt marshes exposed to chronic oilings indicated that there was little long term damage to perennial species of plants but severe damage was noted among some annuals. She also observed that _Spartina_ sp. and _Puccinellia_ sp. were more sensitive to the long-term effects of oil than _Juncus_. In contrast, Thomas (1973), found extensive mortality of _Spartina alterniflora_ in lagoons and of the macroalga _Fucus spiralis_ on a rocky shore even two years after a spill of Bunker C oil.

Physical-Chemical Properties of Surfactants

By definition, a surface active agent (surfactant) is a compound that has an oil compatible (lipophilic) and water compatible (hydrophilic) group, which serves to lower the tension at the surface of contact between phases (Schwartz and Perry 1949). Common surfactants are detergents, emulsifiers, wetting agents and dispersants. Although most authors used these terms interchangeably, there are subtle differences as Lindblom (1978) noted:

1. dispersants function to encourage the breaking-up and scattering of another material;

2. detergents physically remove unwanted substances from a solid surface; and

3. emulsifiers promote a stable distribution of one liquid phase in another liquid phase (i.e., oil in water).

Common surfactants can be classified into the following types based on their hydrophilic moiety (Becher 1957):

1. Anionic

    a. soaps such as long-chain fatty acids (e.g., sodium oleates)
    b. sulfated oil or sulfated alcohols (e.g. sodium lauryl sulfate)
    c. petroleum sulfonates (e.g., dodecyl benzene sulfonate)

2. Cationic

    a. amines or quarternary ammonium salts (e.g., cetyl trimethyl ammonium bromide)

3. Nonionic

    a. ethoxylated alkyl phenols (e.g., nonyl phenol-ethylene oxide)
    b. ethoxylated linear alcohols (e.g., oleyl alcohol - ethylene oxide)
    c. esters formed by the reaction of fatty acids with polyhydric alcohols.

Dispersant Types

The three basic types of dispersants are "water-based" products, "solvent-based" products and "concentrates" (Lindblom 1978). Water-based products tend to require more time to effect complete dispersion, depending on the dose or concentration used. Solvent-based products, which are used primarily to disperse waxy or heavy oils, cause dispersion to occur somewhat more easily but require higher dosage, since they lose efficienty if applied in a water-diluted stream. So-called "concentrates", especially the "self-mix" type, break oil into extremely fine droplets, and require minimal physical agitation. All these actions are dependent on the nature of the oil treated, the application method used, and the degree of mechanical agitation.

Exact chemical compositions of commercial oil spill dispersants are closely guarded by the manufacturers. However, the following table provides a basic categorical description of common dispersants, most of which are on the E.P.A. product data acceptance list (Table 3). This list was compiled to provide general information on many commercial dispersants, however product data acceptance does <u>not</u> constitute approval for use. Data is submitted by the manufacturers, who utilize private consulting firms to perform any necessary tests.

Mechanism of Dispersant Action

Under the influence of gravity, oil has a driving force to spread, with the rate of spreading being governed by the interfacial and viscous drag forces opposing it (Ministry of Defence Working Party 1973). The following formula from Canevari (1978), describes this:

$$So/w = \gamma w - \gamma o/w - \gamma o$$

where So/w is the spreading coefficient, γw is the surface tension of water, dynes /cm, $\gamma o/w$ is the surface tension of oil and water, dynes/cm and γo is the surface tension of oil, dynes/cm.

A positive spreading coefficient (So/w) for a particular oil indicates that it will spread easily over the water's surface, whereas a negative value indicates that an oil will spread sluggishly or not at all. Addition of a dispersant increases the spreading coefficient. This is achieved by the dispersant molecule locating and arranging itself at the oil/water interface, with its lipophilic component orienting the oil, and its hydrophilic part orienting to a water molecule. The consequence of this arrangement is the lowering of interfacial tension, which reduces the mixing energy needed to facilitate dispersion (Canevari 1969, 1977, 1978).

Table 3. Common Oil Spill Control Chemicals (A. Humphrey, U.S. EPA, personal communication)

Product	Category	EPA data acceptance
Corexit 7664	water based, non-ionic	Yes
Corexit 8667	hydrocarbon based, non-ionic	Yes
Corexit 9527	self-mix concentrate, anionic	Yes
Corexit OC-5	hydrocarbon based oil collector	Yes
Shell Oil Herder	hydrocarbon based surface collector	Yes
NOSCUM	biological & trace nutrient additive	Yes
Seamaster NS-555	water based, non-ionic	Yes
Gold Crew	water based, non-ionic/anionic	Yes
Atlantic-Pacific	water based, non-ionic	Yes
Cold Clean	hydrocarbon based, non-ionic	Yes
BP-1100X	hydrocarbon based, non-ionic	Yes
CONCO Dispersant K	water based, cationic	Yes
BP-100WD	water based, non-ionic	Yes
Oil Spill Remover	hydrocarbon based, surface collector	Yes
Slick-a-way	water based, anionic	Yes
Petrodeg 100	biological additives	Yes
Petrodeg 200	biological additives	Yes
Proform Pollution control agent	water based concentrate, anionic	Yes
Ameroid oil spill dispersant/LT	concentrate, non-ionic	Yes
Arcochem D-609	hydrocarbon based, anionic	Yes
Holl-Chem 622	NO DATA AVAILABLE	No
Polycomplex All	"	No
Seasweep	"	No
E-314	"	No
Actusol	"	No
Petrolite W-1439	"	No
Jan-Solv 60	"	No
Spill X	"	No
F.O. 300B	"	No
Ridzlik	"	No

Dispersant Effectiveness

Manufacturers have widely proclaimed that dispersants provide fast, efficient mitigation of oil spills. "We wouldn't sell them if they didn't work" (Lindblom, EXXON Corp., personal communication). Numerous authors have questioned this (Gaines 1971; Ruel et al. 1973; Wells and Keizer 1975; Doe and Wells 1978).

It is necessary to realize that several external parameters influence dispersant performance: characteristics of the oil treated (including its interfacial tension properties), degree of turbulence or mixing energy, the dispersant-to-oil ratio, temperature, dispersant application and contact time, and oil slick thickness (Mackay et al. 1978).

The intrinsic effectiveness of a given dispersant is completely dependent on its ability to lower the interfacial tension between oil and water and thus disperse the oil (Silsby 1968; Canevari 1978, 1979). Although dispersants vary in their chemical make-up and intended application, the results of several experiments with different dispersants generally indicate that the following factors increase dispersion: increased agitation, decreased slick thickness, increased temperature, increased dispersant-to-oil ratio, increased contact time, and decreased viscosity of oil (Murphy and McCarthy 1969; Oda 1969; Mackay et al. 1978; Cormack and Nichols 1978).

Laboratory and field tests have been conducted with brand name dispersants, usually seeking to correlate the amount of chemical needed to disperse a given quantity of oil (Beynon 1969). From these it is apparent that no dispersant works well on weathered oil, that only solvent-based products are effective on very waxy or viscous oils, and that certain brands of dispersants simply work better than others (Gaines 1971; Doe and Wells 1978; Cormack and Nichols 1978; Wells and Harris 1979). Indeed, Tables 4 and 5 suggest that most dispersants are ineffective against any oil heavier than a light Venezuelan crude.

Methods and Logistical Problems of Oil Spill Control

Of the known methods available to mitigate the effects of an oil spill, only two warrant serious consideration: mechanical and chemical controls. However, before employing either or both techniques there are a number of factors that must be considered to decide which is the most suitable. Among these are the location, size and type of oil in the spill; the proximity of the spill to land; wind, wave and current conditions; type and amount of equipment available for clean-up; time required to do the clean-up job; personnel requirements; and ecological considerations (Exxon 1979; Fraser 1979; Lindstedt-Siva 1979).

Table 4. Effectiveness of dispersants tested in freshwater and seawater (in brackets) using the Simulated Environment Tank (SET) test. Each value represents the mean minimum dispersant to oil ratio required to disperse at least 65 percent of the test oil. The term IE means the dispersant was ineffective under the particular set of conditions (after Doe and Wells 1978).

Dispersant	Temperature, °C	Mean Minimum Dispersant-to-Oil Ratio			
		No. 2B Furnace Fuel Oil	Venezuelan Lago Medio Crude Oil	Medium Bunker Fuel Oil	Heavy Bunker Fuel Oil
1. "Self-mix" dispersants					
Corexit 9517	5	1:10	1:1	IE(1:3)	IE(1:1)
	15	1:10	IE	....	....
Corexit 19-L-50	5	....	1:1	IE(1:10)	IE(1:10)
	15	....	1:1	....	....
2. Concentrate dispersants					
Corexit 9527	1	....	1:10(1:27)	(IE)	(IE)
10% dilution of Corexit 9527	1	....	1:1(1:3)	....	....
Synperonic OSD 20	5	....	1:1(1:27)	(1:1)	(IE)
	15	....	1:9	IE	(1:1)
10% dilution of Synperonic OSD 20	5	....	IE(1:1)	(IE)	....
	15	....	IE(1:3)	(IE)	....
3. Water-immiscible conventional dispersants					
BP1100X	1	....	1:3(1:3)	....	....
	5	....	1:3(1:3)	IE(IE)	....
	15	1:10	1:10	....	....
Corexit 8666	1	....	IE(IE)	....	....
	5	1:10	IE(1:1)	(IE)	....
	15	1:10	IE	....	....
Drew Chemical OSE 71	1	....	1:10(1:3)	IE(IE)	....
Drew Chemical OSE 72	1	....	1:9(1:3)	IE(IE)	....
Oilsperse 43	1	....	1:3(1:3)	....	....
	5	1:10	1:10(1:9)	(IE)	....
	15	1:10	1:10	IE	....
Shell dispersant LTX	5	....	1:1(1:3)	IE(IE)	....
	15	1:10	1:10	....	....
4. Water-miscible conventional dispersants					
Corexit 7664	5	IE	IE	....	....
	15	IE	IE(IE)	....	....
Linco-6	5	1:3	IE	....	....
	15	1:10	IE	....	....
Sugee #2	5	IE	IE(IE)	....	....
	15	1:3	IE	....	....

Table 5. Effectiveness of oil dispersants (after Wells and Harris 1979).

10:1 OIL:DISPERSANT	% OIL DISPERSED
Corexit 9527	38.8 ± 7.1
Oilsperse 43	10.3 ± 1.5
BP1100X	9.0 ± 1.0
DREW OSE 71	2.5 ± 0.7
H_2O Diluted Corexit 9527	2.0 ± 0
Corexit 8666	0
Control	0

Mechanical Procedures

Due to the known toxicity of most dispersants, several authors have suggested that dispersant should not be used under conditions that allow for mechanical recovery of spilled oil (Coit 1978; Cowell 1978; Gundlach *et al*. 1978; Lindblom 1978, 1979). The rationale behind mechanical methods is physical containment of the oil in a given locality within a barrier boom. After containment, skimmers or addition of sorbent materials and their subsequent removal will, presumably, extract the oil from the water body. It may then be possible to reprocess this oil for future use (Smith 1978; White *et al*. 1979; Milgram 1979).

In an offshore situation where high energy winds, waves, and currents are prevalent, the effectiveness of booms, skimmers and other mechanical means of oil recovery is severely reduced. Under such conditions dispersant use for the control of spills may be warranted, if clean-up attempts are advisable at all (Garnett and White 1978; Lindblom 1978; Manolio and McCarthy 1978).

Several different types of commercial booms (Ayers 1977; McCracken 1978; Vanderkooy 1978), sorbent materials (Strozeski and Dewling 1969; EPS 1978) and skimmers (Anon. 1977, Breslin 1978; Smith and McCracken 1978) are available for the effective recovery of spilled oil. However, all these items suffer from one or more serious drawbacks such as high cost, large size, heavy weight and unreliability (Meikle and Solsberg 1979).

Dispersant Usage Procedures

Important considerations for dispersant usage are: dosage rate (proper volume of dispersant per unit area), correct dispersant type for the chemical composition of the particular oil (*e.g.*, only solvent-based products work on waxy oil), and efficient distribution of dispersant onto the oil with subsequent mixing (Allen 1978; Garnett and White 1978; Lindblom 1979). When attempting to control an oil spill, the primary concern is to get the dispersant onto the oil. Workboats and aircraft fitted with spray-booms are capable of delivering a sufficient dose of chemical to a large area, with aircraft having the advantage of speed (Allen 1978; Cormack and Nichols 1978; Lindblom 1979; Wiman 1979).

Water-based products and concentrates are usually applied via eduction into a sea-water stream, while solvent-based products must be dispensed undiluted. A spray system using high volume for boats (100 to 150 gal/min) or for large aircraft (350 gal/min), and using a high pump pressure (80 to 100 PSI), is desirable (Lindblom 1978).

Excluding the "self-mix" concentrates, dispersants require mechanical agitation to effect dissolution and scattering of an oil slick. This can be achieved with propeller turbulence and boat wake, towed mixing gates, or natural wave action (Cormack and Nichols 1978; Manolio and McCarthy 1978).

Finally, a problem frequently overlooked when using dispersants to control oil spills is cost. The theoretical cost to disperse 20,000 m^3 of oil is $10.22 million or $511/$m^3$, not including manpower, shelter, food, airstrip development and other assorted costs (Ross et al. 1978). It has been estimated that during the recent Campeche Bay blowout in the Gulf of Mexico, over a quarter of a million gallons of oil dispersant had been used at the well head. The dispersant used costs $8.00 a gallon, exclusive of all transportation costs (G. Lee, FDER, personal communication). Obviously, the expense involved may limit the employment of dispersants.

Effects of Dispersants

Toxicity Test Procedures

Toxicity bioassays have played an important role in the attempt to gauge the deleterious effects of oil and oil dispersants in the environment (Tarzwell 1969; Doe and Wells 1978). In a bioassay, experimental organisms are subjected to a series of concentrations of a known or suspected toxicant under adequately controlled conditions (Am. Pub. Health Assoc. 1971). Acute bioassays measure the concentration of pollutant necessary to produce death in 50% of the test organisms (LC50), usually within 96 hours (Doudoroff et al. 1951; Ruel et al. 1973). Sprague and Carson (1970) have formulated this general rule of thumb regarding toxicity of oil and dispersants: 1-100 ppm = toxic; 100-1000 ppm = moderately toxic; 1000-10,000 ppm = slightly toxic; 10,000 and up = fairly non-toxic.

The primary uses of these short-term toxicity test are to answer general questions such as: (1) Is it toxic?, (2) How toxic?, (3) Does it vary in toxicity?, (4) Which fractions of the material are most toxic?, (5) Do treatment methods and dilution effectively protect the aquatic biota? (Sprague 1973). Other important uses of acute toxicity tests are to determine the relative sensitivity of various species and their life stages to a pollutant, to develop criteria for establishing water-quality standards, and to determine the variable toxicity of a substance due to synergistic effects (Craddock 1977). Since petroleum treated with dispersant is generally too complex for its toxicity to be measured on an individual chemical basis, a bioassay evaluates the mixture in its entirety in the quickest most economical way (Henderson and Tarzwell 1957).

Table 6. Acute toxicity of petroleum to marine animals (after Moore, Dwyer and Katz 1973)

Organism	Material Tested	Lethal Concentration
		ppm
Finfish	Soluble hydrocarbons	5-50
Larvae and eggs		0.1-1.0
Pelagic crustacea		1-10
Benthic crustacea		1-10
Gastropods		10-100
Bivalves		5-500
Other benthic invertebrates		1-10
Finfish	No. 2 fuel oil/kerosene	550
Larvae and eggs		0.1-4.0
Pelagic crustacea		5-50
Benthic crustacea		5-50
Gastropods		50-500
Bivalves		30,000-40,000
Other benthic invertebrates		5-50
Finfish	Fresh crude oil	88-18,000
Larvae and eggs		0.1-100
Pelagic crustacea		100-40,000
Benthic crustacea		56
Gastropods		?
Bivalves		1,000-100,000
Other benthic invertebrates	Fresh crude oil	100-6,100
Finfish	Gasoline	91
	Diesel fuel	240-420
Finfish	Waste oil	1,700
Larvae and eggs		1->25
Pelagic crustacea		15->50
Finfish	Residual oils	2,000-10,000

Table 7. Acute toxicity of water-soluble fractions of a crude and refined oil to marine species from four phyla (after Rice et al. 1975; Rice, Short and Karimen 1976)

Organism	Avg. 96 hr. TLm (ppm) of WSF[a] of:	
	Crude Oil	No. 2 fuel oil
Echinodermata Sea Cucumber (2 spp.)	10.8	2.3
Mollusca 10 species	9.8	2.3
Arthropoda Crabs (4 spp.) Shrimp (5 spp.)	2.3	2.3
Amphipod, Isopod, Mysid, and Barnacle (1 sp. each)	8.5	4.1
Chordata Fish (5 spp.)	1.8	1.8

[a]WSF: Water-soluble fraction.

Acute Oil Toxicity

The results of numerous bioassays indicate that the toxicity of petroleum varies according to several factors (Craddock 1977). Crude oils are generally less toxic than refined oils. Refined oils, such as No. 2 diesel oil, are more lethal because of an increased content of aromatic hydrocarbons, such as naphthalenes, which are soluble but have low volatility (Shelton 1971; Anderson *et al.* 1974; Vanderhorst *et al.* 1976b). For example, gasoline and kerosene are among the more toxic refined petroleum products (Van Gelder-Ottway 1975a). The lower boiling point and highly water soluble fractions of crude oils are responsible for most acute toxicity noted with these oils (Baker 1971c; Wells and Sprague 1976).

Fresh oil is more toxic than weathered oil since weathered oil loses most of its volatile saturated hydrocarbons and low boiling point aromatics via evaporation (Cowell 1969; Van Gelder-Ottway 1975a). Results of toxicity tests have suggested that toxicity increases directly with increasing soluble polycyclic hydrocarbon or benzene content (Myerhoff 1975; Tatem *et al.* 1978).

However, an oil slick floating on the open ocean and not subjected to voilent agitation is generally not too harmful, due to the lack of contact of the oil with aquatic life (Swedmark *et al.* 1973; Van Gelder-Ottway 1975b). Elgerschuizen and DeKruijk (1976) report LC_{50}'s of >100,000 ppm for the stoney coral, *Madracis mirabilis*, subjected to different crude oils floating on the water surface of its environment. Tables 6 and 7 provide acute toxicity data for a variety of marine organisms exposed to different types of oil.

Acute Dispersant Toxicity

Bioassays performed on first generation dispersants (Torrey Canyon era) proved them to be extremely toxic, often because of the hydrocarbon based solvents they contained (Bellan *et al.* 1969; Shelton 1969; Crapp 1971a,b,c). Portmann and Connor (1968) tested the lethality of eleven of these first generation dispersants on 3 species of decapods and 1 species of mollusk. The following table (Table 8) summarizes their results: (The larvae of each species were more sensitive (susceptible) by at least a factor of 10.)

Industry's later efforts results in formulation of many less toxic products, the so-called second and third generation dispersants (Norton *et al.* 1978). Doe and Wells (1978) determined LC_{50} values for several of these products as a part of a Canadian dispersant evaluation project (Table 9).

U.S. EPA has compiled a chart of 48-hour LC_{50} values using *Artemia* (brine shrimp) as the test organism, from product data supplied by the manufacturers of recent dispersant formulations (Table 10).

Table 8. Acute toxicity of some first generation oil dispersants (after Portmann and Connor 1968).

48 hr LC_{50} (ppm)				
1st generation dispersant	PINK SHRIMP *Pandulus montagui*	BROWN SHRIMP *Crangon crangon*	SHORE CRAB *Carcinus maenas*	COCKLE *Cardium edule*
Slickgone 2	4.5	3.5	21.3	30.5
Slickgone 1	5.2	6.6	35.0	32.4
BP 1002	5.8	5.8	15.0	81.0
Essolvene	8.6	9.6	17.5	63.0
Polyclens	8.5	15.7	23.2	70.0
Gamlen D	11.5	9.6	--	38.8
Gamlen OSR	12.5	8.8	20.4	15.8
Slix	12.1	114.5	>15.0	12.7
Cleansol	32.0	44.0	102.0	19.2
Atlas 1901	87.2	120.0	>150.0	48.5
Dermol	148.0	156.0	435.0	148.0

Table 9. Acute lethal toxicity, expressed as 4-day median lethal concentrations (LC_{50}), of dispersants to fingerling rainbow trout determined by screening toxicity tests. Ranges denote concentrations causing 0 and 100% mortality, respectively (after Doe and Wells 1978).

Dispersant	4-Day LC_{50}, mg/litre
1. Passed screening test	
BP1100X	3600 (range: 1800 to 5600)
Corexit 8666	>10000
Corexit 9517	180 (range: 100 to 320)
Corexit 9527	260 (range: 100 to 560)
Corexit 19-L-50	380 (range: 100 to 1000)
Drew Chemical OSE 71[a]	3200 (range: 1000 to 10000)
Drew Chemical OSE 72[b]	3200 (range: 1000 to 10000)
Linco-6	>1000
Oilsperse 43	>1000
Shell Dispersant LTX	750 (range: 560 to 1000)
Sugee #2	>1000
2. Failed screening test	
Actusol T-766	14 (range: 7.5 to 24)
Duosol	<24 (60% mortality at 13)
Energy Plus	57 (range: 32 to 100)
Misco "No Flash"	18 (range: 10 to 32)
Momar OSR	<10
Nokomis-3	75 (range: 56 to 100)
Synperonic OSD 20	80 (range: 32 to 100)

[a]Now marketed as Drew Chemical Oil Spill Dispersant LT.
[b]Not marketed in Canada as of mid-1977.

Table 10. EPA product data list (A. Humphrey, U.S. EPA, personal communication)

Product	*Artemia* sp. 48 hr LC_{50} (ppm)
Corexit 7664	990,500
Corexit 8667	1.7
Corexit 9527	40
Seamaster NS-555	>100,000
Gold Crew	630
Atlantic Pacific	60
Cold Clean	210
BP-1100X	8
CONCO dispersant K	300
BP-1100 WD	1.2
Oil Spill Remover	780
Slick-A-Way	14.5
Proform Pollution Control Agent	330
Ameroid Oil Spill/LT	5.5
Arochem D-609	240

It is evident that these products vary widely in toxicity, but there seems to be a direct relationship between increased dispersant effectiveness and increased lethality (A. Humphrey, EPA, personal communication; Swedmark *et al.* 1973). As an example, Corexit 7664, with a reported LC_{50} of 990,500 ppm (Table 10), was proven completely ineffective against Santa Barbara crude (Gaines 1971). In contrast, Corexit 9527, which has a high effectiveness rating is also considered quite toxic (Table 10) (Wells and Harris 1979).

One should note the reported, unusually high LC_{50} value of 990,500 ppm for Corexit 7664. Other scientific investigators (Gaines 1971; McManus and Connel 1972) obtained LC_{50}'s of 7,200 ppm and 1,200 ppm respectively, for the same product. However, the type and age of organisms used may profoundly influence the test results. For example, fish larvae are much more sensitive than adults to toxicants (Wilson 1977; Portman 1968) and crustaceans, bivalves and teleost fish exhibit a wide disparity in lethal response to the same dispersant (Swedmark *et al.* 1971).

Acute Toxicity of Oil Plus Dispersant Mixtures

Virtually every author who has investigated the toxicity of oil plus dispersant mixtures reports dramatic increases in mortality when compared to oil or dispersant alone, indicating the existence of supra-additive synergism (George 1971; Conner 1972; Swedmark et al. 1973; Linden 1975; Wells and Keizer 1975; Elgerschuizen and DeKruijf 1976; Doe and Wells 1978). This more-than-additive toxicity also occurs when surfactants are combined with heavy metals (Calamari and Machetti 1973).

Linden (1975) found that dispersed oil (BP1100X or Finasol OSR 2 + Venezuelan crude) was 50 to 100 times more toxic than the oil alone to herring larvae. Elgerschuizen and DeKruijf (1976), working with a stoney coral, determined an LC_{50} of 38,550 ppm for Shell Dispersant LTX, and LC_{50}'s of over 100,000 ppm for 3 different crude oils. However, when oil and dispersant were combined, an increase in toxicity was readily evidenced by the resulting LC_{50} values of 182 ppm, 202 ppm, and 726 ppm for each of the 3 different oil plus dispersant mixtures. Using cod as a test animal, Swedmark (1974) ascertained 96 hour LC_{50} values of 940 ppm for a dispersant, 1000 ppm for Oman crude oil and 120 ppm for a 1:1 mixture of the two. Avolizi and Nuvazhid (1974) report deleterious effects of Corexit 7664 and oil on bivalves even though the Corexit 7664 is less toxic than most dispersants. Other researchers report increased toxicity due to oil plus dispersant mixtures in green algae (Heldal et al. 1978), brown shrimp (Norton et al. 1978), crustaceans and subtidal mollusks (Simpson 1968), and fish (Baldini and Cugurra 1974). Tables 11 and 12 summarize the results of other investigators that demonstrate the toxicity of oil plus dispersant mixtures when compared to either oil or dispersant.

Physiological Mechanisms of Dispersant Toxicity

Several authors have speculated on the physiological mechanisms behind dispersant toxicity. The more plausible of these are that dispersants: 1) upset the ion balance and osmoregulation in bivalves or the respiratory organs in fish and decapods (Swedmark et al. 1971), 2) block the central nervous system in fish (Wildish 1973), and 3) reduce oxygen tension at the gills causing asphyxiation (Wilson 1977).

Granmo and Kollberg (1976) exposed cod (*Gadus morrhua*) to 5 ppm of a non-ionic surfactant, nonylphenol ethoxylate. After eight hours, tissue concentrations of the surfactant rose to over 100 ppm in the gills and intestines, 500 ppm in the kidneys and liver, and 4000 ppm in the gall bladder. Fish revived in fresh seawater could eliminate a maximum of 60% of the toxicant, meanwhile exhibiting a high rate of mortality. The investigators concluded that the cause of acute surfactant poisoning was due to the swelling of the gill lamellae and changes in membrane permeability, bringing on asphyxiation.

Goldacre (1968) exposed amoeba to anionic, cationic and non-ionic surfactants to study their effects on the cell membrane. Results indicate that these chemicals adsorb to the membrane or compete for adsorption with an existing membrane component, leading to lysis and death of the cell. The findings of Anastasin and Jelescu (1973) agree with this.

Table 11. Acute lethal toxicity, expressed as 4-day median lethal concentrations (LC_{50}), of dispersants and dispersant-oil mixtures to fingerling rainbow trout determined by definitive toxicity tests. Each 4-day LC_{50} represents an individual toxicity test (after Doe and Wells 1978).

Dispersant	4-Day LC_{50}[a], mg/litre	
	Dispersant	1:1 Mixture of Dispersant and No. 2B Fuel Oil
1. Passed definitive toxicity test		
BP1100X	2078;2440;2900	170; 215; 300
Corexit 8666	6400;29,000;39,360	>100; 117; <320
10% dilution of Corexit 9527	>1800	99; 140; 141
Drew Chemical OSE 71	1800	180
Drew Chemical OSE 72	1100	110
Oilsperse 43	<1000; 749; 928; 1185; 1296	82; 105; 110; 130
Sugee #2	>5600; 9100	132; <180
2. Failed definitive toxicity test		
Corexit 7664	490; 720; 851	<56; 65; 107
Corexit 9517	240	52
Corexit 9527	140; 150; 170; 223	35; 46; 52; 65
Linco-6	1350; 1750	<75; 79
Shell dispersant LTX	360; 471	110; 180
Synperonic OSD 20	50; 51; 76	48; 80; <100
10% dilution of Synperonic OSD 20	605	193

Table 12. Per cent dead sea urchins at 96 hours exposed to oil and oil plus dispersant (after Wells and Keizer 1975).

Replicate	Oil/Dispersant	Oil	Control
1	80% dead	0%	0%
2	60% dead	0%	0%
3	100% dead	0%	0%
4	50% dead	0%	0%

In a realistic oil spill clean-up situtation, it is more likely that organisms would be subjected to varying concentrations of dispersed oil in the water column, rather than dispersant alone. Numerous authors state that dispersed oil is much more toxic than oil alone, or dispersant alone, because of its increased availability to aquatic biota and subsequent assimilation (Blumer 1969; Nelson-Smith 1972; Swedmark et al. 1973; Swedmark 1974; Linden 1975; Wells and Keizer 1975; Elgerschuizen and DeKruijf 1976; Doe and Wells 1978).

Shelton (1969) reported that dispersant use on oil slicks increases the tainting of commercial shellfish and lobster. Other studies have proven oil/dispersant combinations to damage respiratory organs in both fish (McKeown and March 1978b) and bivalves (Avolizi and Nuvazhid 1974). McKeown and March (1978a), using rainbow trout, compared the tissue accumulation of chlorine-labeled bunker C oil with a mixture of dispersant (Oilsperse 43) and the same Bunker C oil over a 24-hour period. The fish subjected to the 150 ppm oil/dispersant mixture showed a drastic increase of hydrocarbon accumulation over those in the 150 ppm concentration of oil alone. Tissue hydrocarbon increases of 20-fold in the kidneys; 10-fold in the liver and 7-fold in muscles were all attributed to the action of the dispersant plus oil combination. The authors confirmed the rapid movement of dispersed oil across the gill structures of fish, and its subsequent interaction with blood proteins, allowing for transport through the organism. This experiment demonstrates a mechanism by which dispersed oil is more toxic and can lead to more serious chronic effects than non-dispersed oil.

Some authors have noted the limitations of laboratory toxicity tests when estimating lethality under field conditions (Ruel et al. 1973; Norton et al. 1978). Vandermeulen and Hemsworth (1977) report a significant difference between the "laboratory LC_{50}" and "ecological LC_{50}" of the unicellular alga, Monochrysis lutheri, exposed to concentrations of Kuwait crude oil. While the 24-hour laboratory LC_{50} was 10 ppm, increased mortality due to predation by grazing copepods was detected at 0.1 ppm, suggesting that field conditions severely complicate isolation of mortality due to the chemical alone.

Vanderhorst et al. (1976a) and La Roche et al. (1970) criticized the lack of a standardized method for mixing oil in water in oil bioassays. Under laboratory conditions, the use of violent agitation for such mixing leads to oil-in-water dispersion which have unrealistically high toxicity (Tarzwell 1970; Anderson et al. 1974; Stainken 1976a). Mackay et al. (1978) have since described Simulated Environmental Tanks utilizing a vortex air blower to reproduce natural wind wave agitation. It is probable that oil plus dispersant mixtures prepared with this apparatus would more accurately reflect those mixtures formed under natural conditions. Other authors have also urged the use of more standardized test organisms (Zillioux et al. 1973; Doe and Wells 1978).

A promising avenue of study is water column analysis and sample collection under a dispersed slick at sea (Frankenfeld 1973; Cormack and Nichols 1977; Brown et al. 1978). Samples obtained at various depths could be used to run bioassays, or the concentrations determined could be correlated with existing bioassay data and possibly indicate toxicity of dispersed oil as a function of depth in the water column. This would allow regulatory agencies to set standards regarding use of dispersants at various water depths. Preliminary studies indicate that dispersed oil will be mixed in the upper 5-10 meters of the water column (Johnson 1979). However, the possibility exists that concentrations of dispersed oil sufficient to cause chronic effects may be found at deeper depths. It has been determined that short term exposure to dispersants can cause sub-lethal effects which appear weeks after the initial exposure (Shelton 1969). Landner et al. (1977) stress that the sub-lethal consequences of oil pollution are too frequently overlooked, but may represent the most severe damage to the ecosystem, due to long term interferences with growth and reproduction.

Long Term Effects of Dispersants and Oil Plus Dispersant Combinations

Although petroleum and dispersants by themselves have many acute and sub-acute effects on aquatic ecosystems, numerous authors have found that a combination of the two produces worse consequences, both short and long term (George 1971; Templeton 1971; Renzoni 1973; Mulkin-Phillips and Stewart 1974b; Swedmark 1974; Linden 1975; Van Gelder-Ottway 1975b; Lacaze and Villedon de Naide 1976; Lonning and Hagstron 1976; McKeown and Marsh 1978a, b). The increased toxicity of the oil plus dispersant combinations is primarily the result of the dispersant making the oil components more available (through finely dispersed particles) to aquatic organisms (Swedmark et al. 1973; Elgerschuizen and DeKruijf 1976; Venezia and Fossato 1977; Doe and Wells 1978; Norton et al. 1978).

Use of dispersants may result in two problems:

1) They cause immediate chemical toxicity in affected biotic populations and,

2) They produce more subtle long term problems such as removal of predators or grazers which frequently allows the increased growth of nuisance forms, particularly certain intertidal periphytic algae (Crapp 1971 a, b).

Mommaerts-Billiet (1973) has also suggested that irreversible modifications in morphology or physiology (i.e. mutations) may result from the exposure of organisms to sublethal concentrations of oil plus dispersants.

Studies on the effects of dispersants on bacterial populations are limited and somewhat contradictory. Jones (1968) found that detergents would suppress nitrification and inhibit the growth of chemo-organotrophs and that the detergent molecules themselves were rather persistent. In contrast, Mulkins-Phillips and Steward (1974b) tested four dispersants alone and in combination with crude oils and found none to be toxic or inhibitory to bacterial populations even at the highest concentration tested (1.25%).

Laboratory tests of marine algae subjected to various dispersant and oil combinations showed a variety of results. Ukeles (1965) observed inhibition of growth in unicellular algae subjected to cationic, anionic and non-ionic dispersants. Although some species were only slightly affected by anionic and non-ionic dispersants, all species Ukeles tested were extremely sensitive to the cationic dispersants. Significant growth reductions were observed in Gymnodinium breve (Kutt and Martin 1974) and Phaeodactylum tricornutum (Lacaze and Villedon de Naide 1976) upon application of dispersants. Additionally, several authors (Clendenning and North 1960; Lacaze 1974) have shown a greatly reduced rate of photosynthesis and primary productivity in algal and giant kelp populations subjected to dispersants and oil plus dispersant combinations. Brown (1972, 1973), studying the marine lichen Lichina pygmaea, showed that C^{14} fixation was strongly inhibited or arrested by the fatty acid diethanolamides and nonylphenol ethylene oxides that constitute the surface active agents of the dispersant tested.

The consequences of oil and dispersants that enter salt marshes have been examined extensively by Cowell (1969), Baker (1971a,b) and Baker and Crapp (1971). These authors found that oil alone penetrates the marsh sediments only to a depth of 1 cm. They also noted that oil may produce deleterious effects on Spartina or Puccinellia plants when the shoots are covered and oxygen diffusion into the plants is prevented. However, the use of dispersants greatly magnified the toxic effects of oil as well as any toxic effects the dispersant may have by allowing extreme penetration into the soft marsh sediments. Indeed, Cowell (1969) observed that 50% more Spartina plants died in experimental plots sprayed with oil and dispersant compared with a control plot sprayed with oil alone. All the above authors strongly recommended that dispersants not be used in marsh areas and that other clean-up methods such as burning and the use of sorbent materials (to soak up the oil) be discouraged as well.

The determination of the effects of dispersants and dispersant plus oil combinations on aquatic animals has been restricted primarily to laboratory acute toxicity tests covered earlier in the text. Chronic effects of dispersant use are less well understood due to the lack of long-term ecological studies on the subject. However, available evidence suggests that, as with plants, animal populations suffer more when subjected to dispersant plus oil combinations than with either alone (e.g. Lonning and Hagstrom 1976).

Venezia and Fossato (1977) found that the toxicity of a crude oil to the copepod Tisbe bulbisetosa was reinforced when the dispersant Corexit 7664 was applied. Lonning and Hagstrom (1976) and Hagstrom and Lonning (1977). noted that the dispersant Corexit 9527 produced pathological abnormalities in sea urchin eggs and larvae at concentration as low as 0.0003 ppm. Lewis (1971) found a Corexit brand dispersant to produce more harmful effects in reef corals he studied than oil alone. Foret-Montardo (1971) tested twelve dispersants on the polychaete Scololepis fuliginosa and found that only two of the products showed any decrease in toxicity with time (≤28 days)--suggesting the persistant nature of many dispersants. Bellan et al. (1972) investigated possible sublethal effects of a detergent on the polychaete Capitella capitata and found that survival of juveniles was markedly decreased, number of females decreased, number of eggs laid decreased and development time increased with increasing detergent concentrations. Wilson (1968 a, b) tested the effects of the dispersant BP1002 on larvae of the polychaete Sabellaria spinulosa. He noted that at a concentration of 1 ppm the dispersant only irritated the larvae and they appeared to recover when the solvent fraction evaporated. However, the larvae died several weeks later whereas the controls lived considerably longer. Experiments by Morton and Wus (1977) with two barnacle species (Balanus amphitrite and B. variegatus), and several dispersants, showed that larval forms were killed or their activity reduced at much lower concentrations than were adults. It has also been observed that cationic surfactants were most toxic to nauplii of the barnacle Elminius (Wright 1976). Hargrove and Newcombe (1973) noted that the crawling and respiration rates of the intertidal snail Littorina littorea were increased in the oil alone, but were significantly reduced with brief exposure to a so-called "low toxicity" dispersant (Corexit 8666). Long term exposure (5 months) of the mussel Mytilus edulis to low concentrations (0.5 - 1.5 ppm) of a non-ionic surfactant inhibited or delayed development, but did not hinder spawning ability (Granmo and Jorgensen 1975). Different life stages of the crab Rhithropanopeus sp. were exposed to varying concentrations of anionic and non-ionic detergents (Czyzewska 1976). The results indicated that average larval life span was decreased significantly with increasing detergent concentration. The investigator found that surfactants are adsorbed on the respiratory epithelium causing gas exchange disorders, particularly in the motile forms that respire more rapidly. Evans et al. (1977) observed abnormalities in the feeding behavior of the brown shrimp, Crangon crangon, subjected to concentrations of several dispersants in the range of 1-100 ppm. The shrimp, however, generally recovered after 4 hours in clean water. Kiceniuk et al. (1978) found that it was possible to induce brachycardia in marine fish with low concentrations of a variety of dispersants. Although the effects were dose dependent and reversible, Kiceniuk et al. postulated that this stress, as well as environmental stresses, would produce a debilitating effect that could impair swimming performance and thus make the fish more susceptible to predation. Wildish (1974) and Wilson (1976) noted similar effects with Pseudopleuronectes americanus (winter flounder), Clupea harengus (herring), Pleuronectes platessa (plaice) and Solea solea (sole) when these fish were exposed to various concentrations of a variety of oil dispersants. Both authors also suggested that impairment of swimming ability would allow affected fish to be more susceptible to predation and loss of feeding opportunities. Eisler (1975), in his study of oil and dispersant usage in the Red Sea, found sublethal effects of oil plus dispersant mixtures which included reduction in feeding rate and egg deposition in predatory gastropods, interference with substrate attachment by mussels, liver enlargement and lowered blood hematocrits in fish and bioaccumulation of crude oils in octocorals. He concluded that such materials may disrupt established feeding - predator patterns, reproductive processes and defense mechanisms and therefore constitute a potential threat to population stability.

HISTORICAL PERSPECTIVES

The following historical summaries of three major oil spills provide examples of the results that can be expected when dispersants are used in emergency field conditions.

Torrey Canyon:

On March 18, 1967, the supertanker Torrey Canyon went aground 15 miles west of Lands End, Cornwall, U.K., discharging its total capacity (117,000 tons) of Kuwait crude oil into the sea (Smith, J. 1968). Ten thousand tons of dispersants (mainly BP1002) were used to clean the 13,000 tons of oil that hit the shore (Walsh 1968). Dispersant use proved to be extremely deadly to most intertidal species including grazing mollusks, leading to severe ecological imbalance from excessive growth of the green alga, *Enteromorpha*, and the perennial brown alga, *Fucus* (Southward and Southward 1978). This disaster was the classic case of clean-up doing more harm than the original oil pollutant (Bellamy 1967). Southward and Southward (1978) have stated that despite the popular misconception of rapid recovery, it has taken a full 9 - 10 years for the Cornwall area ecosystem to approach what was once normal.

Brazilian Marina:

In January 1978, the tanker, Brazilian Marina, struck rock in Sao Sebastiano Channel, Brazil, losing 10,000 tons of its Kuwait crude oil cargo. Prevailing winds and currents carried the oil into the coastal embayments and beach areas of Sao Paulo and Rio de Janeiro. Over twenty thousand liters of Bras-X-Plus dispersant were applied to the oiled beaches, effecting a good cosmetic clean-up. However, dispersants caused the oil to penetrate as much as 60 cm into the underlying sand, thus compounding the pollution and aesthetic problems attributable to the spill. Beaches not treated with dispersant, exhibited oil penetration to a maximum depth of 5 cm (Dewling and Silva 1979).

Amoco Cadiz:

On March 16, 1978, in Brittany, France, the Amoco Cadiz, a 233,690 ton capacity tanker, ran aground, spilling 220,000 tons of Arabian light and Iranian light crude oils (Bellier and Massart 1979). Due to extremely rough seas and strong winds, the oil quickly formed a water-in-oil emulsion ("chocolate mousse") containing 50% to 80% water (Wolfe 1978). A total of 1300 metric tons of various dispersants (BP1100X, Finasol OSR 2, BP1100WD, Finasol OSR 5) were used by the French Navy, but they proved very ineffective against the viscous "mousse" (Bocard et al. 1979). The high seas hindered mechanical removal, and subsequently large amounts of the water-in-oil emulsion came ashore, impacting 220 kilometers of beaches and intertidal areas (Hann 1979). Massive mortalities of intertidal organisms occurred, including several million mollusks and urchins, 3200 marine birds, and thousands of polychaetes and crabs (Cross et al. 1978). Cross et al. also reported fish kills that may have resulted from dispersant use, but the full extent that these chemicals contributed to mortalities was not known.

DISPERSANT TREATED OIL SPILLS VS. UNTREATED SPILLS

The question of whether to treat an oil spill with chemical dispersants or not is a difficult one to answer since each spill poses unique circumstances such as oil type, local weather and tidal conditions as well as distribution and type of marine organisms (Wilson 1978; White *et al.* 1979). Even the Exxon Corporation, one of the largest manufacturers of oil dispersants state in their dispersant advertising literature:

> "Chemical agents are not recommended if physical means of removing the oil are feasible, or if time is not a major factor. Location, weather conditions, water currents, and type of oil product spilled must also be considered." (Exxon 1979).

Based on field studies of four major oil spills and a review of pertinent literature, Gundlach *et al.* (1978) categorized coastal areas as to their vulnerability to oil spills as well as to various clean-up techniques:

1. Exposed, steeply dipping or cliffed rocky headlands - oil rarely impacts due to high energy backwash and therefore no clean-up would be required.

2. Eroding wave cut platforms - no clean-up necessary.

3. Flat, fine sand beaches - oil by itself, penetrates only a few centimeters. Clean only the high tide wash line.

4. Steeper, medium to coarse grained beaches - oil may mix deeper, 50 - 100 centimeters. Clean-up is difficult and should be restricted to the high tide wash zone only.

5. Exposed, compacted tidal flats - Biological damage may be heavy. Clean-up only if quantity of oil is extreme.

6. Mixed sand and gravel - penetration and burial of oil is rapid and deep. Oil is very persistent and clean-up impossible.

7. Gravel beaches - oil penetrates up to 65 centimeters. Clean-up will cause beach erosion.

8. Sheltered rocky coasts - biological damage may be severe, but clean-up will do more harm than good.

9. Sheltered estuarine tidal flats - biological damage may be severe, but clean-up will do more harm than good.

10. Sheltered estuarine salt marshes and mangrove coasts - serious, long term (>10 years) effects that are impossible to remedy.

It seems evident that once an oil spill reaches a coastline there are few areas in which any clean-up technique would be feasible or even possible. If dispersants must be employed, the intertidal regions are obviously not the place for their use.

Wilson (1978) produced a table listing the effects that one would expect if a spill was left untreated or treated (Table 13). The one item that is not stressed in Wilson's table is the well-known fact that untreated oil is much less toxic by itself than in a dispersant mixture (Simpson 1968; George 1971; Conner 1972; Norton et al. 1978). The data some companies have submitted on the use of oil dispersants in actual spill situations suggest that little or no ecological damage occurs (Canevari 1975, 1979; McAuliffe et al. 1975). The position that oil company scientists and their consultants take concerning dispersant use is that untreated oil spills, subject to wave and wind generated turbulence, would form an oil in water emulsion that is very stable and resistant to degradation (Canevari 1975; Mackay et al. 1979). If dispersants were used immediately following a spill, they reason, the formation of this emulsion would be prevented and the dispersed oil would be allowed to rapidly dissipate.

However, as Lindstedt-Siva (1979) has suggested, the primary considerations for cleaning up oil spills should not be aesthetic, rather they should be based upon minimizing ecological damage. Many cleaning techniques such as the use of dispersants, steam cleaning or burning may remove visual evidence of oil, but concurrently these methods kill or severely damage the biotic community in the affected area.

Additional considerations for the use of dispersants have been noted by the Australian government when they investigated various methods for combating oil spills (Kerr et al. 1974). They found that, generally, highly effective dispersants were also the most toxic and vice versa. The result of their search was to choose the most effective and toxic dispersant.

In conclusion, from an ecological standpoint, the use of dispersants should not be permitted once an oil spill has reached the shoreline. It seems evident that the use of dispersants in this instance only exacerbates the effects of petroleum toxicity. This does not preclude the use of these chemicals in deep offshore waters where rapid dilution of the dispersed oil is possible. It is also necessary that if they must be employed, dispersants be used as soon as possible after a spill occurs to take advantage of their useful properties. It is recommended that, due to the evident toxicity of dispersants, their use be prohibited except in deep offshore waters when the possibility exists that an oil spill may come ashore.

Table 13. Treated and untreated spills: comparison of effects (after Wilson 1978).

Untreated Spill	Treated Spill
(1) Drifting and spreading oil slick continually moving over new water	Since treating agents disperse the oil into the water column, the dispersed oil will move with the water column
(2) Microbial utilizations	Microbial utilization increases with dispersion
(3) Suspended sediment transport and sediment contamination	Sediment transport and sediment contamination should be reduced because of cleansing properties of dispersant
(4) Toxicity - generally limited to surface and benthic zone	Thought to increase in water column in vicinity of spill with rapid decrease as oil disperses
(5) Evaporation - primarily a function of oil spill, surface area, and wind-wave activity	Effect of treating agents on the rate of evaporation not known
(6) Dissolution and emulsification	Use of a treating agent probably does not increase solubility but does increase the amount of oil that is dispersed into the water column. The more stable water-in-oil emulsions have been shown to be less likely to occur when dispersants are used

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