

Recovery of Oil Spills by Dispersants in Marine Arctic Regions

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By

Asmaa Ali Shata

Supervisor: Asc. Professor Kåre B. Jørgensen



**University of
Stavanger**

Department of Mathematics and Natural Sciences

Faculty of Science and Technology

University of Stavanger

Stavanger, Norway

Foreword

The work presented in this research has been carried out at the department of organic chemistry at the University of Stavanger. I would like to thank my advisor prof. Kåre Jørgensen for excellent supervision, continuous support, constructive collaboration and concrete discussions during the entire period.

It is my pleasure to appreciate and thank my mother and all my brothers and sister for supporting me through my life.

I am really grateful to my husband for his continuous support during this work and my great thanks to my children, Specially Nadin.

Preface

The research deals primarily with dispersants in cold sea water. It brings to the reader well-rounded view of the dispersant situation especially in Norway. There are significant data presented, particularly on the actual use of dispersants, the special permission which is required to use dispersant in Norway and the fact of dispersant effectiveness and toxicity. Many studies have been carried out on the use of dispersants since the birth of the oil spill industry after the Torrey canyon incident in 1968. The effectiveness of dispersants can be measured in the laboratory, there are many differences in the testing procedures but there is some important factors should be considered in the laboratory test such as sea energy and salinity. The toxicity of dispersant and the oil that is dispersed into the water column became an issue in the early 1970s when application of toxic products resulted in substantial loss of sea life. The second generation of dispersants have been less toxic than the earlier ones but there is still a strong polarization between those opposed to dispersant use and those in favour of dispersant use. In general, this report makes a valuable contribution on both sides of the ongoing debate on the use of dispersants.

Abstract

The initial appearance of dispersants was 1960s and 1970s; oil spill dispersants have been the topic of significant research, testing, and debate. In spite of published reports about dispersant toxicity and effectiveness vary greatly, most spill response experts agree that oil spill dispersants are a valuable tool for responding to marine oil spills.

Dispersants are oil spill response chemicals that are used to disperse floating oil into the water column. Dispersant cause a temporary increase in the concentration of oil in the water column, but do not add to the inherent toxicity of oil. Dispersants are effective in getting more oil into the water column compared to the amount that enters in the absence of dispersants, but the inherent toxicity of the oil remains the same whether physically or chemically dispersed. By increasing the surface area of oil, dispersants can facilitate biodegradation of oil. Effective of dispersants during the early phases of oil spill response may prevent or reduce impacts to coastal habitats and wildlife. This means that it is important to be prepared before the situation arises. Personnel should be well trained and needed equipment easily available. A pre-made priority list of different geographical areas to protect is a vital tool to make the correct decisions when concentrating the effort. The net environmental benefit of dispersant use need to be weighed against other oil spill response options. Decision makers must consider the potential effectiveness of dispersant treatment as well as the potential for environmental benefits or harm. When dispersant technology progresses, the policy debates among responders, regulatory agencies, researchers, and environmentalists continue to try to define optimal dispersant application conditions while ensuring that this response tool does not aggravate the environmental damage caused by marine oil spills.

Contents

Foreword	II
Preface	III
Abstract	IV
Abbreviations	V
1 Introduction	1
2 The arctic region	3
2.1 Average atmospheric temperatures for arctic areas	4
2.2 Ice formation in arctic	4
3 Oil spill risks and impacts	6
3.1 The composition of oil	6
3.2 Properties of oil	7
3.3 properties of oil in arctic	8
3.4 Effects of oil spills in the environment	9
3.5 Behaviour of oil spill in the environment	13
4 Oil spill response methods and technology	16
4.1 The main categories of oil spill response methods	16
4.2 The debates of dispersants use	19
4.3 Advantages of dispersant use	20
5 Effectiveness of oil spill dispersants	21
5.1 The chemistry of dispersants	21
5.2 The physics of dispersant action	21
5.3 The composition of dispersant which is used in cold sea water	22
5.4 Natural dispersion and the use of dispersants	25
5.5 The factors affects on dispersants effectiveness	27
5.6 The effectiveness of relevant dispersant for use under arctic and sub arctic conditions	28
5.7 How to maximize dispersant effectiveness	29
6 The toxicity of oil spill dispersants	30
6.1 Some factors influencing aquatic toxicity thresholds of dispersants or their component surfactants	30
6.2 Acute toxicity and sublethal toxicity of dispersants	31
6.3 Sites and physiology of toxic action	32
6.4 Chemical dispersants appear to protect organisms in some studies	32
7 Dispersant spraying equipment	33
7.1 Some important functions for the equipment of dispersants	33
7.2 Vessel dispersant application systems	33
7.3: Comparison of Vessel Application Equipment Systems	35
7.4 The most important characteristic of vessels	38
7.5 The operational procedure of dispersant application by vessels	38

7.6 Advantages and disadvantages of vessel dispersant application.....	38
7.7 Aircraft dispersant application systems.....	39
7.8 The operational procedure of dispersant application by aircraft.....	39
7.9 Advantages and disadvantages of aircraft dispersant application.....	40
8 Shoreline cleanup application.....	42
8.1 Physical processes which are influencing oil distribution and persistence near-shore....	42
8.2 A classification of coastal environments.....	43
8.3 Cleanup methods.....	48
9 Oil spill response decision tree and cleanup cost factors.....	50
9.1 Decision-making at the time of the spill.....	50
9.2 Oil spill cleanup cost factors.....	52
10 Oil spill contingency planning and dispersant policy issues in Norway.....	55
10.1 Oil spill contingency planning in Norway.....	55
10.2 Dispersant policy issues in Norway.....	57
11 Conclusions.....	60
Appendix.....	61
Literature.....	70

Abbreviations

AEA: Technology and National Environment Technology Centre.

AOT: Sodium dioctyl sulfosuccinate. Produced by Sino Chemical Industry Co., Ltd.

ANS: Alaska North Slope.

ATCC: Acinetobacter Calcoaceticus.

BIOS: Baffin Island oil spill.

Bunker C: Viscous oil.

BTEX: Benzene, Toluene, Ethyl-benzene and Xylenes.

Corexit 7664: Brand name of a dispersant from Exxon.

Corexit 9500: Brand name of a dispersant from Exxon.

Corexit 9527: Brand name of a dispersant from Exxon

DOR: Dispersant-to-Oil Ratio.

EC₅₀: Effective concentration to 50% of the population.

Gpm: Gallon per minute.

IR: Infra-Red light.

IUPAC: International Union of Pure and Applied Chemistry.

LC₅₀: Lethal concentration to 50% of the population.

Lpm: Litre per minute.

MARPOL 73/78: Marine Pollution 1973 and 1978. See page 57.

NOFO: Operating companies oil spill preparedness on the Norwegian continental shelf. See page 57.

OPRC: Oil pollution, Preparedness, Response and Co-operation. See page 57.

OSCAR: Oil Spill Contingency and Response.

OSIR: Oil Spill Intelligence Report.

OSPAR: Oil Spill Protection and Response. See page 58.

PAHs: Polyaromatic Hydrocarbons.

POE: polyethylene.

SFT: Norwegian pollution control authority. Now currently renamed "Norway climate and pollution agency".

SINTEF-OWM: The foundation for scientific and industrial research-oil weathering model.

SOLAS: Safety of Life at Sea.

Span 80: A brand name for non-ionic surfactant. Produced by Merck Schuchardt OHG

Tween 80: A brand name for non-ionic surfactant. Produced by ICI Americas, Inc.

Tween 85: A brand name for non-ionic surfactant. Produced by ICI Americas, Inc

US: United States.

USA: United States of America.

1 Introduction

As the world population grows and petroleum resources are depleted, increasing attention is being focused on less-accessible supplies, including offshore production in deep water and arctic waters, and to find new hydrocarbons such as methane hydrates that are concentrated in some arctic regions. Increased exploration and production enhances the probability of a spill occurring from offshore platforms as well as spills from associated pipelines, storage tanks and shipping activities. At the same time, changing sea ice conditions are opening new navigational routes. Marine oil spills may result from any phase of oil extraction, storage or transportation. Potential sources of oil spills include well blowouts during sub sea exploration or production, acute or slow releases from sub-sea pipelines, releases from on-land storage tanks or pipelines that travel to water, or accidents involving oil transportation vessels or vessels carrying large quantities of fuel oil. Arctic conditions, such as dynamic ice cover, low temperatures, reduced visibility or complete darkness, high winds, and extreme storms add to the probability of an accident or error that might cause a spill to occur.

The purpose of this research is to document what is currently known about the use of dispersants in cold water to assist decision makers when they face such of these conditions. An extensive review of worldwide scientific and technical journals has been undertaken to identify relevant literature on the use of dispersants for oil spill response in coldwater.

Chapter 2 defines the arctic region and the significant difference in the average temperatures between summer and winter and explain ice formation in arctic.

Chapter 3 deals with oil spill risks and impacts. Topics covered include the composition of oil, properties of oil, properties of oil in arctic, effects of oil spills on the environment, and behaviour of oil in the environment. When oil spills on water, various transformation processes occur that are referred to as the (behaviour) of the oil. There are many types of transformation process are discussed in this chapter such as, evaporation, emulsification, natural dispersion, photooxidation, dissolution, biodegradation, sedimentation, spreading and drifting.

Chapter 4 summarizes the technologies used to physically recover oil spill, using mechanical recovery, in-situ burning, dispersants and manual recovery. The impact of arctic conditions on the effectiveness of mechanical recovery, in-situ burning and dispersants are summarized. Argument of dispersant use and advantages of dispersant use are discussed.

Chapter 5 describes the chemistry of dispersants and the physics of dispersant action. The composition of dispersants which are used in cold sea water is explained. Natural dispersion and the use of dispersants are discussed. Finally the chapter discussed the effectiveness of dispersants.

Chapter 6 discusses the toxicity of dispersants.

Chapter 7 covers the different types of dispersants spraying equipment. The advantages and disadvantages of each technique are discussed.

Chapter 8 discusses the physical processes and different shoreline environments which are influencing oil distribution and persistence near-shore because oil spill on shorelines is more difficult and time-consuming to clean up than spills in other locations, and clean up efforts on

shorelines can cause more ecological and physical damage than if the removal of the oil is left to natural processes.

Chapter 9 deals with Oil spill response decision-making, explains how dispersant use should be considered at the time of a spill. And summarize the impact of oil type, shoreline oiling, location type, spill size, location and clean up strategy on cost.

Chapter 10 discusses oil spill contingency plans in Norway and some international and multilateral agreements which Norway participate in it.

Chapter 11 presents the conclusion.

2 THE ARCTIC REGION

The arctic region can be defined by latitude (the Arctic Circle) or by vegetation, temperature or other geographical or political boundaries. Webster [1] defined it as the region lying north of the Arctic Circle or of the northernmost limit of tree growth; the polar area north of the timber line. Figure (2.1) shows some common delineation of arctic regions. Arctic oil and gas development poses considerable threats and challenges to a region already under stress from a changing climate, accumulating pollutants and other types of resource extraction, (such as oil and gas). The sensitivity of arctic ecosystems to spilled oil is briefly considered [2]. The environmental conditions that contribute to oil spill risks – lack of natural light, extreme cold, moving ice floes, high winds and low visibility – can also make spill response operations extremely difficult or totally ineffective.

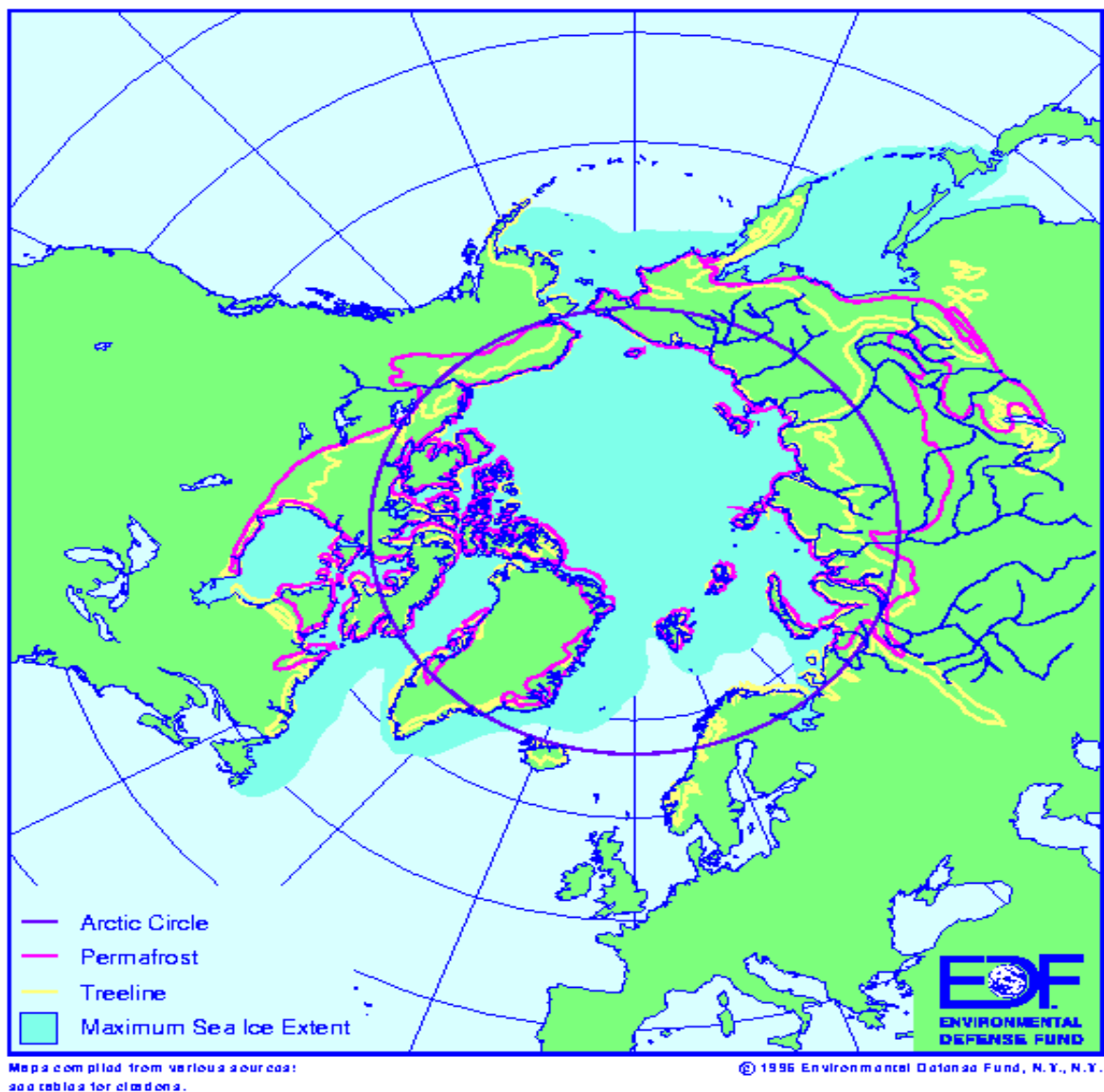


Figure 2.1: Map of the Arctic region showing the Arctic Circle, areas of permafrost, the tree line and maximum sea ice extent [3].

2.1 Average atmospheric temperatures for Arctic areas

There is a significant difference in the average temperatures between summer and winter in the area around the North Pole. In summer there are only two areas with a mean temperature below 0 °C, an elliptical area covering the North Pole and the inner parts of Greenland. During winter there is a much larger area with subzero temperatures. At minimum ice extent, which is in the autumn, the ice covers the areas around the northern part of Alaska, Greenland, and islands north-west in Canada. Also the northern part of Spitsbergen and some areas of northern Russia can have ice in their coastal waters. At this time of year there is no ice in the Finish bay. The period of maximum ice extent is spring time [4].

2.2 Ice formation in arctic

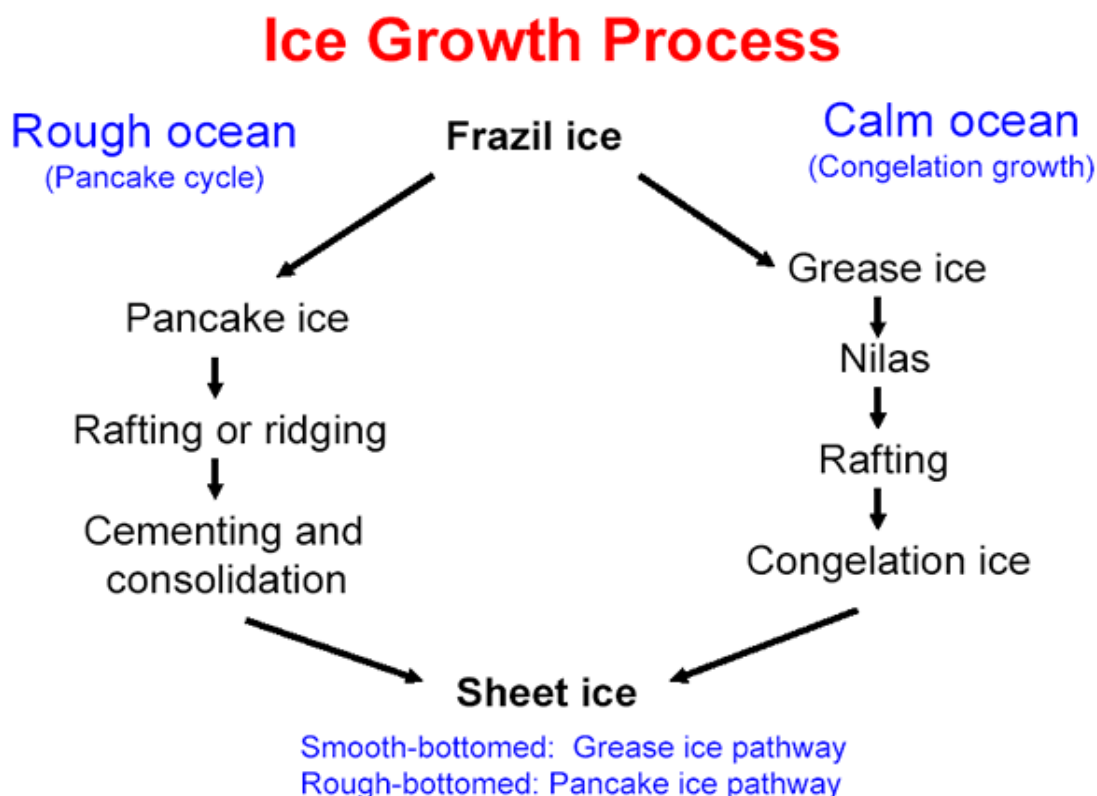


Figure 2.2: Ice growth process [5]

As the ocean water begins to freeze, small needle-like ice crystals called frazil form, figure (2.2). These crystals are typically 3 to 4 millimetres in diameter. Because salt doesn't freeze, the crystals expel salt into the water, and frazil crystals consist of nearly pure fresh water. Sheets of sea ice form when frazil crystals float to the surface accumulate and bond together. Depending upon the climatic conditions, sheets can develop from grease and congelation ice, or from pancake ice. In calm waters, frazil crystals form a smooth, thin form of ice, called grease ice for its resemblance to an oil slick. Grease ice develops into a continuous, thin sheet of ice called nilas. Initially, the sheet is very thin and dark (called dark nilas), becoming lighter as it thickens. Currents or light winds often push the nilas around so that they slide over each other, a process known as rafting. Eventually, the ice thickens into a more stable sheet with a smooth bottom surface, called congelation ice. Frazil ice cannot form in the relatively still waters under sea ice, so only congelation ice developing under the ice sheet can

contribute to the continued growth of a congelation ice sheet. Congelation ice crystals are long and vertical because they grow much slower than frazil ice.

If the ocean is rough, the frazil crystals accumulate into slushy circular disks, called pancakes or pancake ice, because of their shape. A signature feature of pancake ice is raised edges or ridges on the perimeter, caused by the pancakes bumping into each other from the ocean waves. If the motion is strong enough, rafting occurs. If the ice is thick enough, ridging occurs, where the sea ice bends or fractures and piles on top of itself, forming lines of ridges on the surface. Each ridge has a corresponding structure, called a keel that forms on the underside of the ice. Particularly in the Arctic, ridges up to 20 meters thick can form when thick ice deforms. Eventually, the pancakes cement together and consolidate into a coherent ice sheet. Unlike the congelation process, sheet ice formed from consolidated pancakes has a rough bottom surface.

Once sea ice forms into sheet ice, it continues to grow through the winter. When temperatures increase in spring and summer, the first-year ice begins to melt. If the ice does not grow thick enough over the winter, it will completely melt during the summer. If the ice grows enough during the winter, it thins during the summer but does not completely melt. In this case, it remains until the following winter, when it grows and thickens and is classified as multiyear ice [5].

3 OIL SPILL RISKS AND IMPACTS

3.1 The composition of oil

Crude oil are mixtures of hydrocarbon compounds ranging from smaller, volatile compounds to very large ,non-volatile compounds This mixture of compounds varies according to the geological formation of the area in which the oil is found and strongly influences the properties of the oil . Hydrocarbon compounds are composed of hydrogen and carbon, which are the elements in oils. Oils also contain different amounts of sulphur, nitrogen, oxygen, and sometimes mineral salts, and trace metals such as nickel, vanadium, and chromium.

The hydrocarbon structures found in oils are **the saturated compounds**; saturate means the carbons are saturated with hydrogen, figure (3.1). The saturate group consists of alkanes which are compounds of hydrogen and carbon with the maximum number of hydrogen atoms around each carbon. The saturate group also includes cyclo- alkanes. Larger saturate compounds are waxes [6, 7].

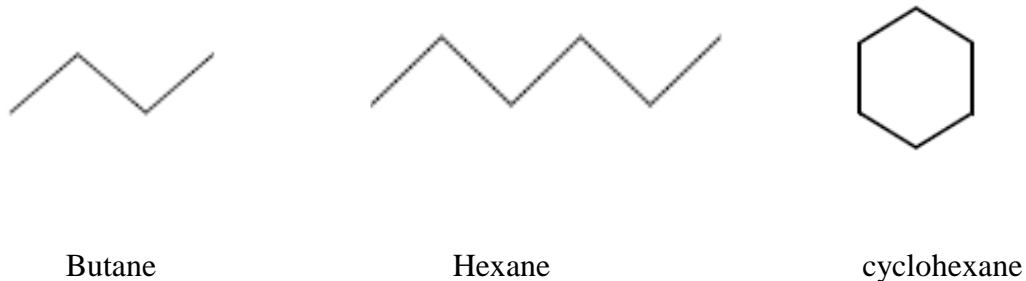
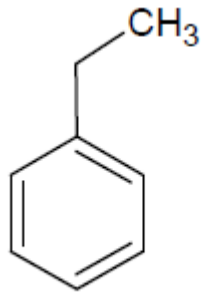


Figure 3.1: Structure of common saturated compounds

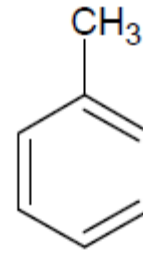
The olefins or unsaturated compounds are compounds that contain fewer hydrogen atoms and have at least one double carbon -to-carbon bond that displaces two hydrogen atoms. For example ethylene (CH_2CH_2).

The **aromatic compounds** include at least one benzene ring of six carbons. Three double carbon-to-carbon bonds float around the ring and add stability. Because of this stability, benzene rigs are very persistent and can have toxic effects on the environment.

BTEX, or benzene, toluene, ethyl-benzene, and xylenes. These compounds are some of the volatile organic compounds found in petroleum, figure (3.2). Toluene, ethyl benzene, and xylenes have harmful effects on the central nervous system [7].



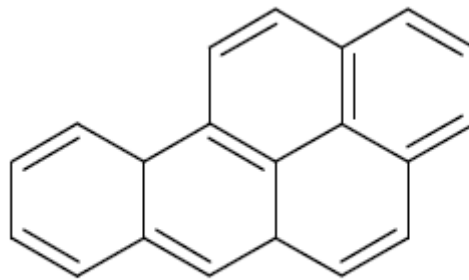
Ethyl benzene



Toluene

Figure 3. 2: Structure of common aromatic compounds

Polyaromatic hydrocarbons (PAHs) are compounds consisting of at least two benzene rings. For example: Benzo[a]pyrene, figure (3.3).



Benzo[a]pyrene

Figure 3.3: Structure of Polyaromatic hydrocarbons

Polar compounds are those that have a molecular charge as a result of bonding with compounds such as sulphur, nitrogen, or oxygen. In petroleum industry, the smallest polar compounds are called “resins” which are responsible for oil adhesion. The larger polar compounds are called “asphaltenes” because they make up the largest percentage of the asphalt used for road construction [7].

3.2 Properties of oil

The properties of the oil can be listed as: [6]

- (1) **Viscosity** is the resistance to flow in a liquid. The lower the viscosity, the more the liquid flow. The greater the percentage of light components such as saturates and the lesser the amount of asphaltenes, the lower the viscosity. Viscosity is affected by temperature, with a lower temperature giving a higher viscosity. In the cleanup of oil spill, viscosity can affect the oil's behaviour. Viscous oil do not spread rapidly, do not penetrate soil, and affect the ability of pumps and skimmers to handle the oil.

- (2) **Density** is the mass of a given volume of oil and is expressed in grams per cubic centimetre (g/cm^3). Density is important because it indicates whether particular oil will float or sink in water. When the density is 1.0 g/cm^3 at 15°C and the density of most oil ranges from 0.7 to 0.99 g/cm^3 , most oil will float on water. The density of oil increases with time, as the light fraction increases.
- (3) **Solubility** is the measure of how much of oil will dissolve in the water column on a molecular basis. The amount of oil lost to solubility is always so small (generally less than 100 parts per million) not like the loss of evaporation which is great.
- (4) **The flash point** of oil is the lowest temperature at which it can vaporize to form an ignitable mixture in air. A liquid is considered to be flammable if its flash point is less than 60°C .
- (5) **The pour point** of oil is the lowest temperature at which it will flow, and if the temperature is decreased the liquid will stop to flow. Pour point had been used to predict how oils will behave in the environment. For example; waxy oils can have very low pour points, but will continue to spread slowly at that temperature.
- (6) **A distillation fraction** is the separation of a mixture into its component parts, or fractions, such as in separating chemical compounds by their boiling point by heating them to a temperature at which several fractions of the compound will evaporate. Each fraction had a higher boiling point than the previous fraction. The distillation fraction had a strong relationship to the composition and the physical properties of the oil.
- (7) **The oil /water interfacial tension** is the force of attraction between the surface molecules of oil and water. The lower the interfacial tensions with water, the greater the extent of spreading.
- (8) **The vapour pressure** of oil is a measure of how the oil partitions between the liquid phase and the gas phase. When the oil weathers, the vapour pressure changes because oils are a mixture of many compounds. Vapour pressure is difficult to measure and is not used to estimate oil spills.

3.3 Properties of Oil in arctic

There are several characteristics of the arctic environment and arctic wildlife species that increase the potentially negative consequence of an oil spill to arctic waters. Population recovery after an incident may be slowed because many species have relatively long life spans and slower generational turnover [8].

There are some positive effects and negative effects of ice. The positive effects are ice floes create barriers for the oil, and the layer will be thicker than a spill in open waters. Emulsion is created at a slower rate inside the ice cover due to the damping of the waves. As evaporation is reduced due to the increased thickness of the oil slick, larger amounts of the lightest components remain in the oil. This makes it easier to ignite, and also less viscous. The time window for action is in this way increased.

The negative effect is the rate of natural dispersion is low at some distance from the edge. There is also no use in applying dispersants, because this still requires some energy for

dispersion to take place, and this energy is not there. Only in case of a rough sea state outside the ice cover, the frequent collision between floes at the outermost border might supply the energy required [9].

Oil persists longer in arctic conditions because it evaporates more slowly or may be trapped in or under ice and is thus less accessible to bacterial degradation. Dispersion and emulsification will usually be smaller in ice because the wave energy is lower than at open sea.

Sea ice has a specific weight of around 0.92. Most of the crude oils have a specific weight between 0.85-0.90 [10], which mean that it floats better than the ice. At Perfectly calm conditions this means that oil will flow over rather than under the ice.

The pour point of oil is usually in between 35°C to -57°C and is partly connected to the amount of waxes that oil contains. If the temperature of the sea is lower than the pour point, the oil will generally not spread on the surface because it has turned into a semi-solid. But it can happen that oils remain liquid at sea temperatures as low as 15 °C below the pour point.

The viscosity of oil is increasing as the temperature decreases. Some of the oils have approximately the same viscosity at 0 °C and 20 °C while others change by an order of magnitude. The density of oil is increasing as the temperature decreases due to the reduced of evaporation when oil is spilled in ice. The flash point will rise at a lower rate because of decreased evaporation [10].

3.4 Effects of oil spills on the environment

Oil spill have many adverse effects on the environment. Oiled birds are obvious effects and there are less obvious effects such as the loss of phytoplankton and other microscopic forms of life.

It will be discussed the actual effects of an oil spill on various elements of the environment such as birds and different species in aquatic environment.

Birds

When the birds come into contact with slicks on water or shorelines, oil contaminates feathers. This is very dangerous for the sea birds because the oiled sea bird loses its body heat, especially at sea and this may cause death. Birds clean their plumage by preening and, may ingest some of the oil. Birds may also ingest oil by eating oiled prey. Ingestion may cause death or cause sublethal effects such as liver problems, gastrointestinal dysfunction, pneumonia and behavioural disorders. When birds ingest only a small amount of oil, they may stop laying eggs or the number of eggs may be reduced. It has been found that a few drops of fresh oil can kill the young in an egg and affect the hatchability of the eggs. Shorelines dwellers and feeders, which include ducks, gannets, and cormorants, are the most susceptible birds to oiling. Auks which spend much of their time on the water are susceptible to oil spills at sea because they feed by diving through the surface [11-14].

In many spills, cleaning stations are set up to rehabilitate birds. Early attempts to rehabilitate oiled seabirds had little success. For example, over 95% of the birds treated after the 1971 San Francisco spill died in captivity [15]. Rehabilitation techniques have improved since then. After the Nestucca spill, One-third (1027) of the (3092) oiled birds found a live on beaches in Washington, after cleaning and returning to sea [16]. Following the Exxon Valdez spill, 50.7% of the 1630 oiled birds received at cleaning stations were released back to the wild [17]. Although techniques have improved greatly in the past few years, success rates are still poor as it is very stressful for a wild bird to be captured and handled. Rehabilitated birds kept in captivity following the normal time of release have been found to suffer a range of

physiological disorders [18], and have lower survival than unoiled controls [19]. Less than half of the oiled birds that are cleaned and released actually survive. Only very sick birds can be captured and brought to the treatment centres are often near death. But at least cleaning birds is easier than cleaning mammals and can reverse some of the effects of an oil spill.

Aquatic Environments

The sea includes a wide variety of ecosystems such as fish, plankton, benthic invertebrates, epontic organisms, marine plants and special ecosystems.

Fish

Aromatic hydrocarbons in the water column will toxic both mid-water and bottom-dwelling fish. Fish species that live close to the water surface, the shore, or the sea floor are the most vulnerable to oil spills. In open seas lethal concentration of oil are rarely found but we can see such concentrations in bays and estuaries. The adult fish tending to be less sensitive than juveniles and juveniles tending to be less sensitive than eggs, but larvae or newly hatched fish are often more sensitive than fish eggs.

Oil exposure can cause sublethal effects such as disruption of growth, decreased assimilation of food, eye cataracts and loss of body weight. In controlled tests, some adult fish species avoided oil slicks on the surface ,but this behaviour has not been observed in open water spills and this is mean some species would avoid an oil spill on open water if they can escape it.

There is no bioaccumulation of hydrocarbons in fish or any other aquatic species because fish and the a aquatic species lose hydrocarbons in almost one year from the time fish are exposed to high sublethal concentrations of hydrocarbons until the level is below detection[20].

Plankton

Plankton are small plants and animals that live in the water and include phytoplankton and zooplankton. Phytoplankton are microscopic plants such as algae and diatoms that live in the top layer of the water as they depend on light for photosynthesis. Zooplankton are microscopic animals that feed on phytoplankton. There are some sublethal effects of oil on zooplankton include narcosis (death-like appearance when the organisms is not actually dead) , reduced feeding, and disruption of normal responses to light.

Plankton are important because they are at the bottom of the aquatic food chain, until it is finally ingested by mammals [21].

Benthic invertebrates

Benthic invertebrates are species live on the sea floor and they are divided into two groups, benthic infauna that reside within the bottom sediments and benthic epifauna that live mostly on the top of the sediments. Benthic invertebrates such as clams, polychaete worms, crabs, shrimp, lobster, and amphipods. Benthic species can be killed by the accumulation of oil on the bottom sediments. This can occur by precipitation down sediment particle or plankton and sometimes if the oil is heavy enough to sink. Larval stages are much more sensitive to oil spill than adults and less mobile species such as starfish, gastropods, and sea urchins are more affected. Sublethal hydrocarbon concentration cause narcosis, slow growth, differential growth of body parts, abnormality in development of organs, reduced feeding and increased respiration. Benthic infauna will sometimes leave their holes, exposing themselves to predators. Starfish will often take back their tube feet and lose their hold as a result.

Benthic invertebrates can take up hydrocarbons by feeding on contaminated material, breathing in contaminated water. When the water and sediment turn to a clean environment, most invertebrates lose hydrocarbons and this can take several months if there is high level of hydrocarbons. Immobile species may die from long time exposure to contaminated sediments [6].

Epontic organisms

Epontic organisms are microscopic plants and animals that live under ice. Epontic organisms are much more vulnerable than plankton, because oil remains under the ice, where these organisms live. Epontic organisms may be slow to recover because the oil can remain under the ice for many months. But there is a limitation of growth for these organisms because the low levels of light and temperature so the dead organisms are not quickly replaced [6].

Marine mammals

The effect of oil spills on marine mammals varies with species. Seals, sea lions, and walruses are vulnerable to oiling because they live on the shore lines of small islands and rocks. External oiling of young seals or sea lions causes death because their coats are not developed enough to provide insulation in an oiled state. Oil is often absorbed or ingested and mothers may not feed their young when they are oiled. Older Seals, sea lions, and walruses can take a large amount of oiling without causing death. Oiling of both adult and young causes the fur to lose waterproofing and buoyancy. Short exposure of Seals, sea lions, and walruses to volatile oil causes eye irritation and long exposure can cause more permanent eye damage.

Whales, dolphins, and porpoises can be exposed to oil in the water column or on the surface when they come up to breathe. But oil does not adhere to the skins of these mammals and they mobile a lot so they are not exposed for a long period of time to oil. Whales and dolphins have been observed to avoid oil spills and contaminated waters.

Polar bears spend much of their time in or near water, swimming between ice floes hunting seals. Polar bears are attracted to oil, particularly lubricating oil, which they will drink and this will cause illness but in the case of an oil spill, it could result in death.

Otters live on or near shorelines and spend much of their time in or near the water, feeding on crustacean on the see floor. Oil adheres to the fur of the otter causing heat loss. After 30% oiling, otter can die. Otters try to clean themselves after oiling and ingest oil and this lead to some inflammation in the stomach. Oiled otters are often caught and taken to rehabilitation centres for cleaning by specialists. Some otters can be saved after cleaning but such rehabilitation is expensive and difficult and many animals die after their release, as a result for human handling [22].

Intertidal fauna

Intertidal fauna include animals that live in the shoreline zone between the high and low tides. These species are the most vulnerable to oil spills because they and their habitat are coated during oil spills. Intertidal fauna include the mobile crabs, snails, shrimp, sessile; mussels, sedentary limpets, periwinkles and tube worms. Most organisms will take up light oil; especially immobile species such as sessile. There are some sublethal effects on crabs and mussels such as reduced growth and reproduction rate and accumulation of hydrocarbons. When mussels and crabs placed in clean water, they will clean themselves of hydrocarbons.

Heavy oiling will generally kill most species. There are two kinds of shoreline cleaning techniques, instructive techniques such as washing with hot water or high- pressure water and this kind of technique can remove many of the food sources and delay recovery, despite removing all of the oil. The other technique is a non-instructive technique such as washing with cold water or low-pressure water and the recovery by using this technique is better more than the previous one because it does not remove the food sources [23].

Marine plants

Marine plants are a different kind of plant families and algae. Intertidal algae, macro-algae, and sea grasses are of special interest during oil spills.

Intertidal algae are an important food source for much of the intertidal fauna and can be severely affected by an oil spill. Intertidal algae grow on rock and sediment surfaces and will re-establish on oil-coated rocks if the oil is weathered and no longer emits volatile compounds. Sublethal effects include reduced reproduction and respiration rates and changes in colour. Using instructive cleaning techniques are not good for intertidal algae and more intertidal algae will be killed by these techniques than by oil.

Macro –algae include two groups of plants in North America, Fucus and kelp. These plants make up the habitat for complex ecosystems including many kinds of animals and algae, the hall ecosystem can be affected if they are damaged. Fucus, which live in the lower intertidal and subtidal zones, are not particularly susceptible to oiling because a mucous coating prevents the oil from adhering to the plant but a heavy oil will cover focus and cause death or sublethal effects. Kelp lives in deeper water and is rarely coated with oil but will absorb hydrocarbons in the water column, if the dose of a few hours will cause a sublethal effect such as leaf loss, colour changes, reproductive slowdown, reduced growth, and accumulation of hydrocarbons and it is the same for focus. But a moderate concentration over a few days could cause more serious damage and even death. In clean water, both plants will clean them selves of hydrocarbons. Recovery for both types of plants and their habitats may take several years.

Sea grasses live in the low-intertidal and subtidal zones and spread a round the world. Sea grasses are sensitive to hydrocarbons uptake. Eelgrass is a common species and is a vascular plant; this plant is very sensitive to hydrocarbons and is killed by moderate hydrocarbon concentration in the water column for a few hours or low concentrations for a few days.

Sublethal effects of eelgrass as kelp and fucus and in clean water eelgrass will lose hydrocarbons. Recovery of eelgrass may take several years [24, 6].

Special ecosystems

Arctic environments are mentioned as a special case for oil spills because the diversity of biota is low and it takes longer to develop and grow. Oil takes longer to degrade and weather in the arctic, toxic. Volatile components are retained longer. Because all these reasons, recovery from an oil spill is slower in the arctic environment than in high temperature and tropical zones.

Coral reefs occupy a large part of the seas in the tropics of the pacific and the Caribbean. Coral reefs support thousands of fish, invertebrate species and algae. Moderate concentrations of hydrocarbons can kill coral and its occupants. Damage depends on the depth, when coral reefs are down to a bout six metre from the surface; it is more vulnerable to oil. There are some sublethal effects on coral, such as slowed growth, slowed respiration and unnatural coloration. Recovery of coral reefs is very slow.

Salt and marches are important ecosystems because they are the habitat of many birds and fish that feed on a wide variety of invertebrates including crabs, snails, and worms. Some of these organisms dig a hole into the sediments, so if there is an oil spill the oil will penetrate the sediment easily. Salt marches are vulnerable to oil spills because they are flooded at high tide and their complex surface traps large quantities of oil and it is difficult to clean up the oil. The effect of oil on a marsh depends on the amount and type of oil. Light to moderate

amounts of oil that does not penetrate the sediment notably will not cause mortality and the marsh can recover in one or two years. Heavy amount of oil that penetrates the sediment notably will cause mortality and the marsh can take up to ten years to recover. Instructive cleanup can cause more damage than the oil itself [6].

3.5 Behaviour of oil in the environment

When crude oil is spilled at sea, the weathering processes start to change the physical and chemical properties of the oil. The properties of the crude oil and the weathering conditions such as temperature, wind speed and sea state are the main factors which control of these changes, figure (3.4) illustrates the weathering processes that occur at the sea.

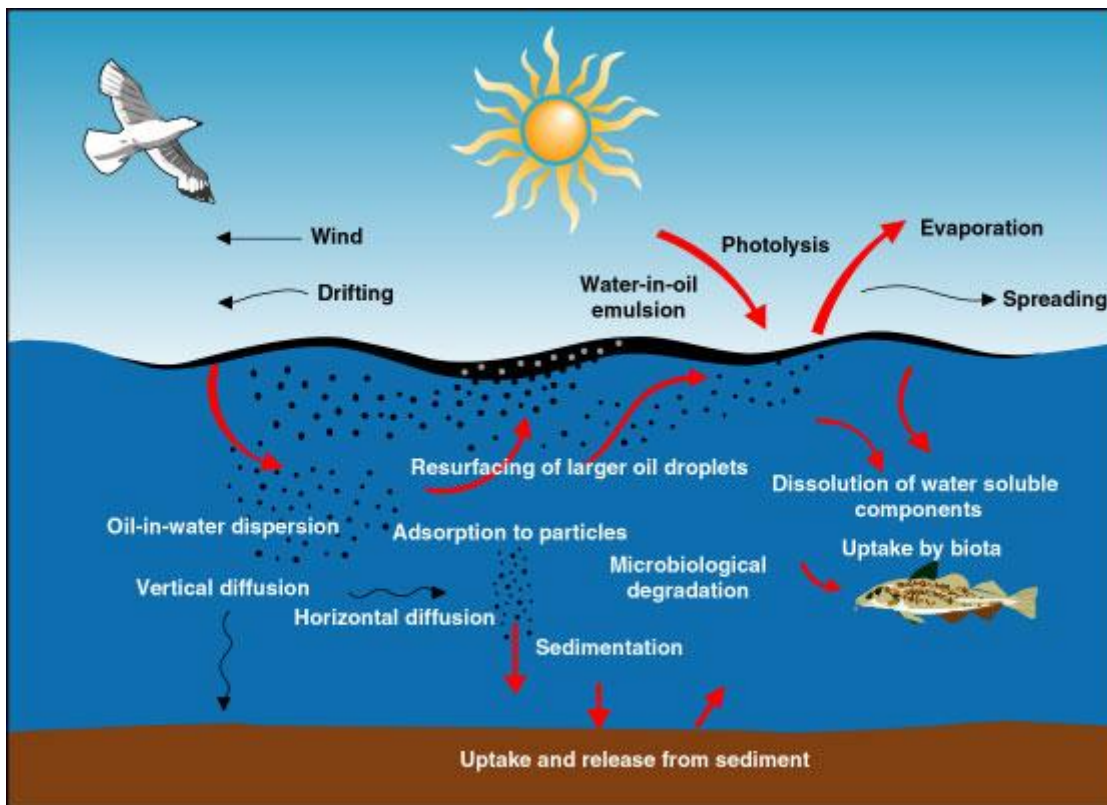


Figure 3.4: Weathering processes of crude oil on water [25]

Evaporation is one of the most important processes that remove oil from the water surface. The rate of evaporation depends on the oils composition. When the oil contain more volatile components, the rate of evaporation will be great. The loss of the more volatile components will cause the remaining oil to have higher viscosity, pour point, and flashpoint than the original crude oil.

Emulsification is the most important process that causes spilled oil to persist at the sea surface. Water droplets can remain in the oil layer in a stable form and resulting water-in-oil emulsion. Any asphaltens and resins in the oil will interact with the water droplets to stabilize them, depending on the quantity of asphaltenes and resins, an emulsion will be formed.

Water can be present in oil in different ways. First, when the percentage of water is small almost 1%, this water does not change the physical or chemical properties of the oil. Second, when water droplets are simply held in the oil by its viscosity to form an unstable emulsion,

by the help of sea's wave action, and when the sea energy decreases, unstable emulsion break down into water and oil within minutes or a few hours. The third way is semi or meso-stable emulsion is emulsions that have properties between stable and unstable emulsions [26]. The reason for meso-stable emulsion is the lacks of asphaltenes to make them completely stable or the oil contain many de-stabilizing materials such as smaller aromatics. Also the viscosity of the oil may be high enough to stabilize some water droplets for a period of time. These emulsions generally break down into oil and water or sometimes into water, oil, and stable emulsion within a few days. Meso-stable emulsion can be red or black in appearance [27].

The fourth way that water exists in oil is in the form of stable emulsions. Sjöblom and fellow researchers [28-32] noted that more stable emulsions result from higher asphaltene contents and that resins appear to make less stable emulsions than do asphaltenes. Several papers [33-38] have reported on their results that asphaltenes are primary responsible for emulsion stability and resins is secondary but essential. And they summarize as follows:

(1) Stable and less-stable emulsions exist.

(2) Emulsion stability results from the viscoelastic films formed by asphaltenes at the oil water interface.

(3) Asphaltenes produce more rigid films than resins.

(4) Stable emulsions might be classified by their dielectric and viscoelastic properties.

(5) Water content does not appear to correlate directly with stability however, very low or very high water contents (< 50 or > 90%) are not correlated with stable emulsions.

(6) Most researchers use visible phase separation to classify emulsions as stable or not and most confirm that this is not an optimal technique.

Emulsions of all types contain about 70% water and thus, when emulsions are formed, the volume of the oil spill more than triples. And the viscosity of the oil increases by 1000 times. The increase in volume and viscosity make cleanup operations more difficult. Emulsified oil is difficult or impossible to disperse. Stable emulsions may take months or years to break down naturally. Emulsions can be broken down with special chemicals to recover the oil with skimmers or to burn it. Emulsion formation also changes the fate of the oil. When oil forms stable or meso-stable emulsions, evaporation and biodegradation appears to slow down, and the dissolution of soluble components from oil may stop [31].

Natural dispersion occurs when fine droplets of oil are transferred into the water column by wave action. Natural dispersion is dependent on both the oil properties and the turbulence of the sea. For example heavy oils will not disperse naturally but light oils which have the saturate contents more than the asphaltenes and resins contents can disperse significantly. In addition, very energetic seas help oil spill to disperse naturally.

Photooxidation can change the composition of oil. It occurs when the UV of sunlight causes oxygen and carbons on the oil slick to combine and form new products that may be resins. The resins may be soluble and dissolve into the water or they may cause water-in-oil emulsions to form.

Dissolution is the process which most of the soluble components of the oil are lost to the water column under the slick. These include some of the lower molecular weight aromatics such as benzene and some of the polar compounds, such as resins. If the spill of oil contains a large amount of soluble aromatic components, then a lot of aquatic organisms can be killed.

Biodegradation is the process which micro organisms in the environment can use petroleum hydrocarbons as a food energy source. The rate of biodegradation depends on the nature of

hydrocarbons, the temperature, the availability of oxygen or other nutrient sources such as nitrogen and phosphate which are available on shorelines and the availability of the oil to the bacteria or micro organisms. The rate of biodegradation can be great on saturates which contain 12 to 20 carbons Aromatics and asphaltenes which have a high molecular weight ,biodegrade very slowly . The rate of biodegradation increase as the temperature rises. Some groupings of bacteria function better at lower temperatures and others function better at higher temperatures. Depending on the availability of oxygen, on land oils such as diesel can degrade rapidly at the surface, but very slowly if at only a few centimetres below the surface. Oil degrades mostly at the interface between soil and the oil on land or at the oil-water interface at sea.

Sedimentation is the process which oil is settled on the bottom of the sea under turbulent conditions in shallow water because of the interaction between the oil and the mineral fines suspended in the water column, thereby the oil is transferred to the water column and if the particles of mineral with oil attached are heavier than water, they will sink to the bottom as sediment. When the oil is on the bottom, it is covered by other sediment and degrades very slowly, so it can be very harmful to the biota which comes in contact with the oil on the sea bottom.

Spreading: Oil spreads horizontally over the water surface even in the complete absence of wind and water currents. This spreading is caused by the force of gravity and the interfacial tension between oil and water. An oil spill will spread quickly after a spill. The outer edges of a typical slick are usually thinner than the inside of the slick at the beginning but after a day or more this effect diminishes. Winds and currents also spread the oil out and speed up the process. Oil slicks will elongate in the direction of the wind and the currents.

Drifting: There is two factors affect the movement of oil slick, the more significant factor is the wind and the current speeds at the time of a spill. The minor factor is Coriolis Effect due to the earth's rotation deviation of a bout 30° to 40° to the right in the northern hemisphere and to the left in the southern hemisphere.

Figure (3.5) illustrates the relation between different weathering processes with time.

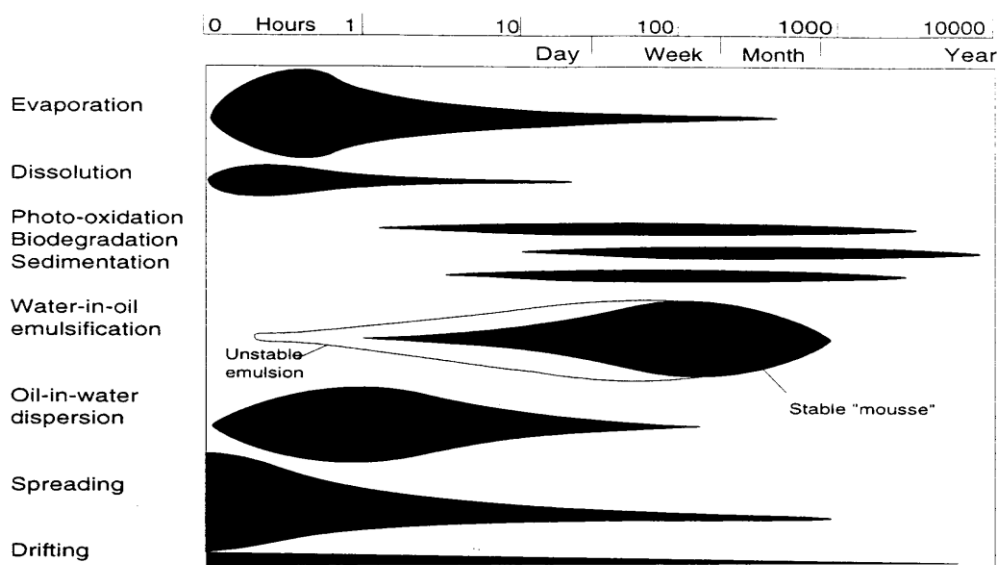


Figure 3.5: Relative importance of weathering processes with time [39]

4 Oil spill response methods and technologies

The arctic environment represents unique challenges to oil spill response technologies and techniques. While in some limited instances, arctic conditions might prove favourable to spill response; in most cases the arctic operating environment reduces the effectiveness of oil spill control and recovery methods and equipment.

4.1 Oil spill response methods are generally divided into three main categories:

1-Mechanical recovery contains the spilled oil using booms, and collects it with a skimming device for storage and disposal. Booms are deployed from vessels or anchored to fixed structures or land. A number of different kinds of skimmers exist; they use suction, oleophilic materials or weirs to remove oil from the water's surface. Once the oil has been recovered, it must be transferred using pumps and hoses to temporary storage until it can be properly disposed of.

Therefore, an effective mechanical recovery system requires that sufficient equipment and trained personnel are available and conditions are helpful to contain, recover, pump, transfer and store oil and oily wastes. Ultimately, all recovered wastes must be properly disposed of according to applicable regulations.

2-Non mechanical recovery which is divided to:

-In-situ burning of spilled oil on the water's surface involves a controlled burn of floating oil that is contained to the appropriate thickness. The oil is ignited by releasing a burning, gelled fuel from a helicopter onto the oil, or by releasing an ignition device from a vessel or other access point. If successfully ignited some or all of the oil will burn off the surface of the water or ice. There will always be some residual non-volatile compounds that remain. This residue may float, sink or be neutrally buoyant depending upon the type of oil spilled and the conditions of the burn.

Successful ignition and burning require enough slick thickness for ignition at least thickness of 2mm to burn on water, minimal wind and waves, and oil that has not emulsified (incorporated water) too much. If a burn is inefficient, a mixture of unburned oil, burn residue and soot will form. As in mechanical recovery, oil containment for ignition can be accomplished either with natural barriers or man-made booms that are both fire-resistant and able to withstand sea ice. Downwind emissions must be below threshold levels for sensitive populations [40]. Chemical groups, currently under development, may thicken a slick to allow for ignition [41].

-Dispersants are a group of chemicals sprayed or applied to oil slicks to accelerate the dispersion of oil into the water column. They do not remove oil from the water, but are intended to limit the amount of oil forming a slick on the water surface or shoreline by driving that oil into a dissolved phase. Dispersants are applied using spray nozzles, pumps and hoses, and can be applied from a vessel or aircraft. Dispersant operations are usually monitored from aircraft to make sure that the application is effective and on target. Dispersants have a limited timeframe for effective application, requiring a prompt, accurate application of the chemicals to the spilled oil with the oil type, emulsification, salinity, weather conditions and sea state all aligned. [2]

3-Manual recovery

Manual recovery is the most common method of shoreline cleanup. Where oil and oiled sediment is removed using simple hand tools and techniques such as pails, shovels forks, sorbent materials, hand bailers or nets. Workers wear protective clothing such as splash suits, boots, gloves and respirators if the oil is volatile. Material is usually collected directly into plastic bags or buckets for transfer. While removing oil manually is a slow process, it generates less waste than other techniques and allows cleanup efforts to be focused only on oiled areas. A disadvantage is the risk of injuries to personnel from falls on slippery and dangerous shorelines.

Most existing oil exploration, production, storage, and transportation operations in arctic waters rely on a combination of mechanical recovery and two major nonmechanical techniques – in-situ burning and dispersant application – to clean up or treat spilled oil.

All three methods require surveillance and spill tracking to identify the location, spreading and condition of the spilled oil in order to select and apply the appropriate response equipment and tactics. All three also require logistical support to transport equipment and trained personnel to the spill site, deploy and operate the equipment, and decontaminate the equipment when response operations are complete. Spill responders must be able to safely access the spill site in order to deploy the equipment.

With all three spill response options, time is critical. As soon as oil is spilled to water, it begins to spread, evaporate and emulsify. As time passes, it generally becomes more difficult to track, contain and recover or treat spilled oil. Therefore, the quick mobilisation and deployment of response equipment and trained personnel is important to the overall response effectiveness.

Environmental conditions in the Arctic are an obvious challenge to the efficacy of most spill response technologies. Typical arctic conditions impacting on oil spill response operations include the presence and type of sea ice, extreme cold, limited visibility, rough seas, and wind. These conditions may also impact on the fate and behaviour of spilled oil, and thus either improve or reduce the effectiveness of response technologies and systems [42].

Table (4.1A) and (4.1B) on the following pages summarises how arctic conditions may impact the effectiveness of mechanical recovery, in-situ burning and dispersant application systems [2].

Table 4.1 A: The impact of sea ice on the effectiveness of different oil spill response methods [2].

Potential impacts on spill response	
Conditions	Sea ice
General constraints	Ice can impede access to the spill area, making it difficult to track and encounter oil. Remote sensing techniques are being improved and refined to detect oil under and among sea ice, but they are not yet mature. Ice can impede or limit vessel operations, especially for smaller work boats. Boats without ice-capable hulls should not operate in heavy ice conditions. Slush ice may clog seawater intakes or accumulate in vessel sea chests.
Mechanical recovery	Containment boom can be moved, lifted or torn by ice. Skimmer encounter rate may be reduced by ice chunks, and skimmers and pumps may clog. Limited manoeuvrability may prevent or delay accurate skimmer or boom deployment. Attempts to deflect the ice from recovery areas may also deflect the oil. Ice must be separated from recovered oil. Ice may provide natural containment. Reinforced vessel hulls or ice scouts may be required. Ice movement can be unpredictable or invisible. Vessel operators must be experienced in the ice conditions of the area.
In-situ burning	Certain ice conditions (i.e.slush ice) may reduce burn effectiveness or impede ignition. Fire boom deployment may become difficult or impossible. Residue recovery requires vessel support. Ice may provide natural containment, and burning in ice leads may be possible.
Dispersants	Oil under ice is inaccessible to dispersant application. Ice can dampen required mixing energy. Dispersants generally less effective at lower salinities. In most regions, dispersants are not considered an operational technology for use in sea ice.

Table 4.1 B: The impact of wind and temperature on the effectiveness of different oil spill response methods [2].

Potential impacts on spill response		
Conditions	Wind	Temperature
General constraints	High winds can make it difficult to deploy effectively the crew, vessels, equipment required for a response. High winds can make air operations difficult or unsafe.	Prolonged periods of subfreezing temperatures can impact personnel safety, or require more frequent shift rotations. Extreme cold temperatures may be unsafe for human operators. Cold may cause brittle failure in some metals. Cold air may freeze sea spray, creating slick surfaces. Icing conditions may make vessels unstable.
Mechanical recovery	High winds can move boom and vessels off station or tear boom off the anchor point.	. Skimmers freeze up. Freezing sea spray can accumulate on boom and cause it to tear, fail or over wash. Increased oil viscosity makes it difficult to recover and pump.
In-situ burning	In-situ burning is not generally safe or feasible in high winds.	Extreme cold temperatures may make ignition more difficult or ineffective, and may cause burn to slow or cease.
Dispersants	Accurate application of dispersants is difficult in high wind conditions.	Cold temperatures and increased oil viscosity may reduce dispersant effectiveness.

4.2 The debates of dispersants use

Although there have been many advances in dispersant formulations and application methods in the last 30 years, planning for dispersant use also needs to overcome some obstacles of perception [43]. An example of arguments that have been used for and against are summarised in the following section. The specifics of the debate have been described in many references [e.g. 43] and only general points are addressed here.

Those opposed to dispersant use:

- It is better to remove spilled oil from the surface of the sea rather than force it into the water.
- The use of dispersants ‘hides’ the problem rather than solving it.
- Addition of chemicals into the environment is undesirable.
- Dispersants are toxic, or their use causes the oil to have greater toxic effect than if dispersants were not used.
- oil will disperse naturally, given enough time.
- Dispersants are an unreliable technique because they do not always work.
- Dispersants are used to avoid the expense of better response options.

Those in favour of dispersant use:

- Environmental damage is caused by exposure to spilled oil. The damage cannot be reversed, but can be minimised by rapid action. Rapid and total removal of spilled oil by mechanical means is rarely feasible.
- Dispersants accelerate a natural process and can provide a net environmental benefit by rapidly removing oil from the surface and thus preventing or minimizing surface and shoreline impacts.
- Many oils exhibit toxic effects whether they are dispersed or not. Modern dispersants have low toxicity and when combined with oil do not add measurably to the environmental effects caused by the oil alone.
- Natural dispersion slows or even stops altogether when the oil emulsifies.
- Emulsified oil poses a long-term hazard to the environment. Dispersants can remove the oil from the surface before it emulsifies and can retard emulsification.
- Like every other response technique, dispersant use cannot be guaranteed to be effective in all circumstances.
- Practical experience has shown that dispersants are one of the few effective response options available.

4.3 Advantages of dispersant use

Dispersants reduce the environmental impact of spilled oil by removing it from the surface of the water, thereby preventing oil from impacting shorelines and sensitive habitats, because oiling of shorelines is environmentally less desirable than dispersing the oil into the water column, where effects are limited and short-lived. So the advantages of dispersant use is provided below [44, 45]

- (1) Dispersants can be used in harsh weather conditions (e.g., rough seas, strong winds and currents). Such conditions can promote dispersant effectiveness. Where mechanical recovery can not be possible.
- (2) Dispersant use allow for rapid treatment of large areas, especially when large fixed wing aircraft are used.

Delay/avoid formation of stable water-in-oil “mousse” emulsions and, in some cases, break emulsions already formed. This emulsification activity Promotes coalescence of the water droplets in the emulsion, which in turn causes separation of water and lowering of viscosity [46, 47].

- (3) Dispersants accelerate the natural biodegradation process by increasing surface area of oil available to bacteria. The dispersants themselves accelerated the process because they themselves are readily biodegradable and stimulate bacterial growth.
- (4) Dispersants make oil less sticky thus decreasing the extent to which oil will adhere to sediment, wild-life, shorelines, vessels; etc. This mechanism prevents oil from ending on the bottom of the sea through attachment to heavier particles and subsequent sinking.

5 EFFECTIVENESS OF OIL SPILL DISPERSANTS

5.1 The chemistry of dispersants

Dispersants are made of surfactants (surface active agents) dissolved in one or more solvents. The characteristic features of a molecule of any detergents are hydrophilic (water-attracting) end and hydrophobic (oil- attracting) end.

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. Low toxicity solvents used in modern dispersants include oxygenated compounds such as glycols and glycol ethers and petroleum-derived nonaromatic hydrocarbons. Some of them 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.

The surfactants used in modern dispersants are generally blends of nonionic and anionic types. The nonionic types include sorbitan esters of fatty acids, polyalkoxylated sorbitan esters of fatty acids, polyalkoxylated fatty alcohols, polyethylene glycol esters of oleic acid and tall oil esters. Anionic type surfactants include salts of dialkyl sulfosuccinates and of alkyl benzene sulfonic acid. [48]

5.2 The physics of dispersant action

As it mentioned before dispersants are made of surfactants dissolved in one or more solvents. When applied to a film of oil, the surfactants diffuse to the oil/water interface. There, they align themselves so that the lipophilic end of the molecule is attached to the oil phase and the hydrophilic end extends into the water phase. This reduces the interfacial surface tension between water and oil and oil is dispersed as tiny droplets. This mechanism is shown in figure (5.1)

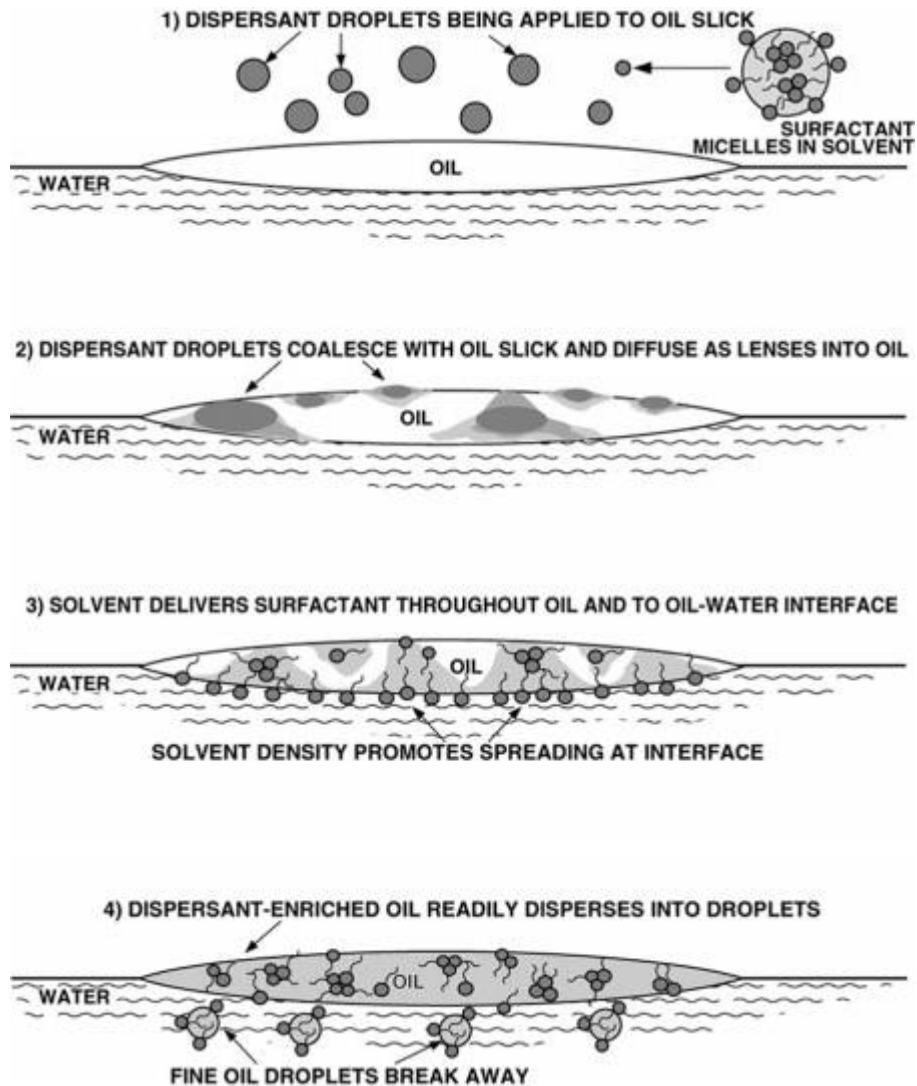


Figure 5.1: Detailed mechanism of chemical dispersion. [48]

5.3 The composition of dispersants which are used in cold sea water

The use of dispersants in arctic and sub arctic waters presents a special set of considerations and concerns. Reduced water temperatures, variations in salinity, and the presence of ice can all impact dispersant effectiveness.

Brown and Goodman [49] tested dispersant effectiveness (corexit 9527 and corexit 9500) in tanks filled with broken ice and water. The researchers found 90% or better dispersion, even when 95% of the water surface was covered by large ice floes. They found that the size distribution of the ice floes had little effect on dispersion.

Researchers at the national marine fisheries service –auke bay laboratory in Juneau, Alaska, USA reported on laboratory effectiveness tests that examined the dispersability of Alaska North Slope under a combination of sub arctic salinities and temperatures, by using (corexit 9527 and corexit 9500). Their results showed an effectiveness of less than 40% for fresh oil and less than 10% of weathered oil. However these results are based on laboratory studies performed at low mixing energy [49]. These results contradict with another study by Ross [50] which concluded that, “if used properly , corexit 9527 should be reasonably effective on spills of Alaska North Slope crude in prince William sound or the gulf of Alaska. ”

Another set of researchers in Alaska determined that minimizing weathering time and applying the dispersant prior to the beginning of mixing was critical to the successful dispersion of Alaska North Slope at 8°C[51].

Corexit 9527 is constitute of about 48% non-ionic surfactants, including ethoxylated sorbitan mono- and trioleates (Tween 80 and Tween 85) and sorbitan monooleate (Span 80), about 35% anionic surfactants, including sodium dioctyl sulfosuccinate (AOT), and about 17% ethylene glycol monobutyl ether as a solvent [52-53]. You may have already noticed that the science surrounding surfactants is somewhat of a black art. For this reason, companies tend to keep secret their industrial recipes that use surfactants. This culture of secrecy surrounding surfactants has led to a large number of trade names. The trade names include things like "Span", "Tween" and letter codes like "AOT".

The following section will include some details about each chemical in Corexit 9527.

(1) Tween 80 (polysorbate 80)

Tween 80 is a non-ionic surfactant and emulsifier derived from polyethoxylated sorbitan and oleic acid, and is often used in foods [54]. Polysorbate 80 is a viscous, water-soluble yellow liquid. The hydrophilic groups in this compound are polyethers also known as polyoxyethylene groups which are polymers of ethylene oxide (figure 5.2 A).

Other names

- Polyoxyethylene (20) sorbitan monooleate
- (x)-sorbitan mono-9-octadecenoate poly(oxy-1,2-ethanediyl) IUPAC name
- Tween 80
- POE (20) sorbitan monooleate

(2) Tween 85

Polysorbate 85 is used as an emulsifier in combination with a variety of other hydrophobic emulsifiers to cover a wide range of oil in water, and water in oil emulsion systems [55]. Individually, it is an excellent solubilizer of vegetable oils and fragrances, a wetting agent, viscosity modifier, stabilizer and dispersing agent (figure 5.2 B).

Other name

Sorbitan trioleate poly (ethylene oxide)

(3) Span 80 sorbitan monooleate [56]

(Figure 5.3 C)

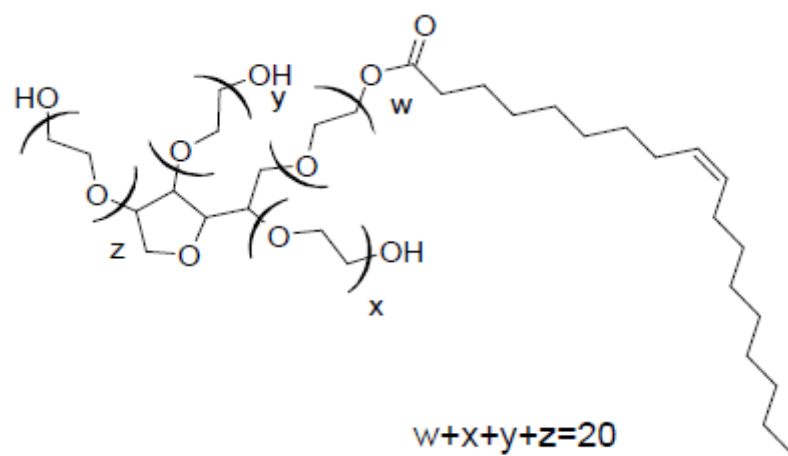
(4) Dioctyl sodium sulfosuccinate [57]

(Figure 5.4 D)

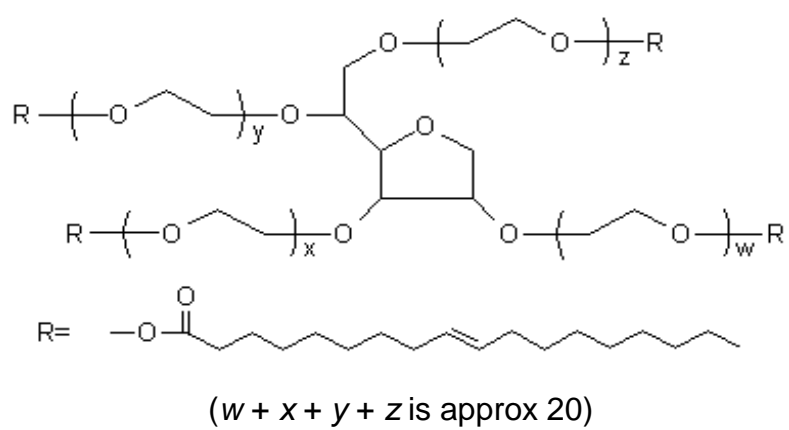
(5) 2-Butoxyethanol

2-Butoxyethanol is an organic solvent with the formula $C_6H_{14}O_2$. It is a colourless liquid with a sweet, ether-like odour. It is butyl ether of ethylene glycol [58]. 2-Butoxyethanol usually decomposes in the environment within a few days and has not been identified as a major environmental contaminant (Figure 5.5 E)

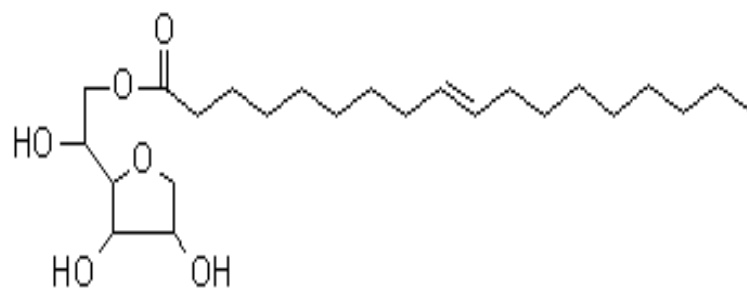
A



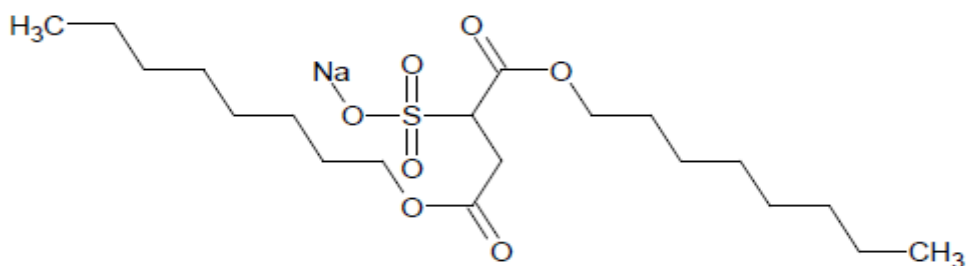
B



C



D



E

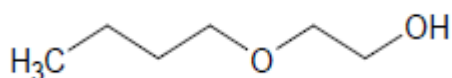


Figure 5. 2: Chemical constituents of

- A) Polyoxyethylene (20) sorbitan monooleate
- B) Sorbitan trioleate poly (ethylene oxide)
- C) Span 80 sorbitan monooleate
- D) Dioctyl sodium sulfosuccinate
- E) Ethylene glycol monobutyl ether

5.4 Natural dispersion and the use of dispersants

When oil is accidentally spilled into the ocean a thin film of oil that spreads under the action of gravitational, viscous and surface tension forces [59]. Evaporation, emulsification and natural dispersion of oil droplets are the three most important factors in determining spilled oil behaviour [60]. Evaporation, such as light fuels (e.g. Gasoline or kerosene) and very light crude will evaporate rapidly for the most part. Both emulsion formation and droplet dispersion involve a process in which small droplets of one phase are created and dispersed into the second phase [61]. So it is important to know the sizes of oil droplets of water-in-oil emulsions. As shown in figure (5.3) small oil droplets with radii of tens of microns have small rise speeds and tend to remain suspended in the water and easily to biodegrade [62]. In contrast, large oil droplets of water-in-oil emulsions with radii of hundreds of micron or larger, will tend to rise to the surface, where the oil can contaminate shore-lines, birds, and marine mammals so small oil droplets are preferred.

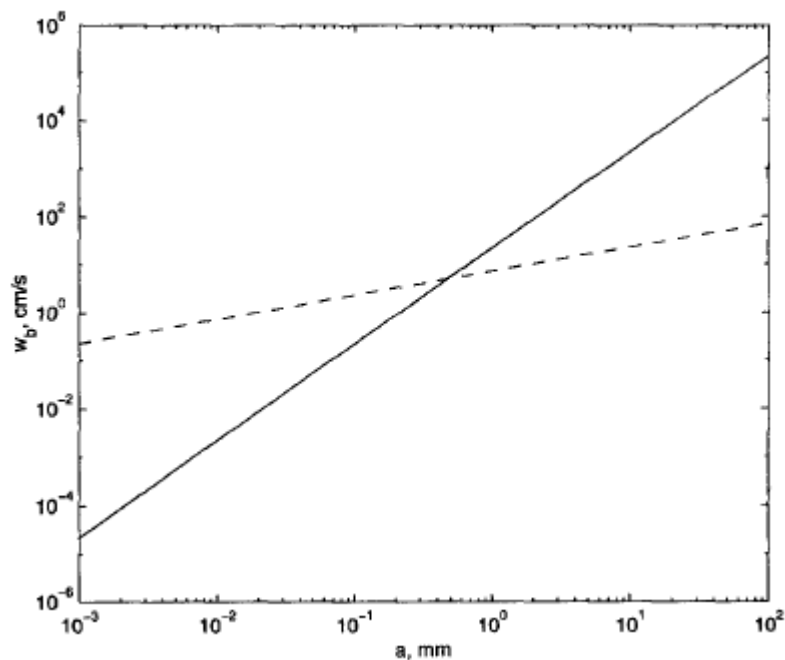


Figure 5. 3: Buoyancy rise speed of oil droplets with density of 900 Kg m^{-3} in water density of 1000 Kg m^{-3} . A solid line at small droplet sizes (droplet Reynolds number $Re < 50$, $a < 0.4 \text{ mm}$), the rise speed varies quadratically with the radius. A dashed line at large droplet sizes ($Re > 50$, $a > 0.4 \text{ mm}$), the rise speed varies like $a^{1/2}$ [62]

There are two kinds of forces to dissipate the oil droplets in the ocean, the first one is the turbulent shear which is the dominant force for the break up and this one generate oil droplets of hundreds of micron in size . These droplets have large buoyancy rise speeds and will rise to the surface after being injected into the water. The second one is the breaking waves especially in rough seas and this one in order to generate smaller oil droplets. But these two forces give a small percentage of the loss of oil to the total volume of the spilt oil [60] but some crude oils will naturally disperse at a rapid rate in turbulent sea conditions. For example, almost all of the 84 000 tonnes (44%) Of Gullfaks crude oil spilled at the *Braer* incident dispersed naturally in the very rough sea conditions [63]. But under normal sea conditions; the majority of crude oils will not disperse, they emulsify and become very persistent on the sea surface and may contaminate the shore. So the use of dispersant permits these oils to be more rapidly dispersed and more readily biodegraded at sea. From figure (5.4) we can see if the magnitude of dissipation rate in the turbulent flow is low [64]. oil droplets are split into big sizes so the droplet Reynolds number become large and this mean that the pressure forces are the dominant force of break up but if the magnitude of dissipation rate of turbulent flow is big, oil droplets will split into small sizes so the droplet Reynolds number become small and this is mean the viscous shear takes over the pressure force in determining droplet break up. Using chemical dispersants in low dissipation rate shifts the droplets break-up from the pressure regime to the viscous shear regime with sizes at (10) micron in size, these oil droplets can remain suspended in the water column in moderate and stormy sea conditions.

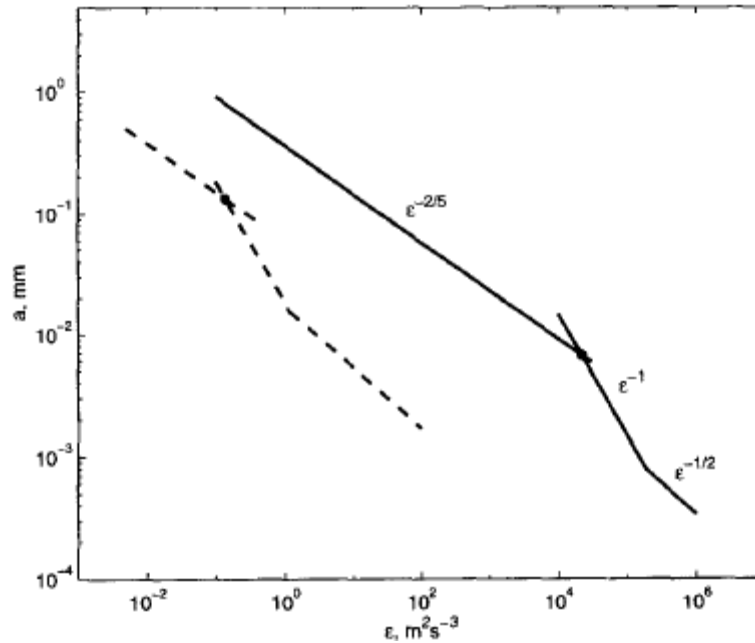


Figure 5.4: Two regimes of oil droplet sizes (solid lines) for an example Of Prudhoe bay oil which has dynamic viscosity $\mu_d=0.1 \text{ kgm}^{-1}\text{s}^{-1}$ Density $\rho_d=900\text{kgm}^{-3}$ and oil-water interfacial surface tension $\gamma =10^{-2} \text{ KgS}^{-2}$, the dashed lines correspond to $\gamma =5 \times 10^{-4} \text{ KgS}^{-2}$ when chemical dispersants are used. The solid dots represent the transition points from the pressure regime to the shear regime [64].

So the chemical dispersants are effective in promoting permanent dispersion of small oil droplets into the water column and prevent or reduce the amount of damage that the surface Oil would cause if driven ashore by winds.

5.5 The factors affects on dispersants effectiveness

There are some important factors affects on the dispersant efficiency such as:

- (1) The composition of the dispersant product.
- (2) The application system.
- (3) The composition and the state of the oil being dispersed.
- (4) The amount of mixing energy in the system.
- (5) The ratio of dispersant to oil.

Of all the factors, mixing energy plays a very significant role on dispersion. [65-67] it helps in the breakage of the floating oil slick as droplets, in the transportation of droplets into the water column, in the breakage and coalescence of dispersed oil droplets [68-72]. Higher energy conditions will increase the rate of oil dispersion, or, alternatively, allow effective dispersion at lower DOR (the ratio of dispersant to oil) [48]. Oil composition can vary , from light crude oils which can evaporate easily, 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. In addition, the oil can become emulsified

with water, causing a significant increase in volume and viscosity. So, (DOR) will increase the rate and degree of oil dispersion. A DOR of about 1:20 is generally used in many standard laboratory effectiveness tests to compare dispersant performance [73]. But as I said before higher energy conditions will increase the rate of oil dispersion, or, alternatively, allow effective dispersion at lower DOR. So the overall treatment ratio of dispersant to oil depends on the circumstances. For example, DOR from about 1:60–1:100 were found to be effective if the oil is light or medium and the sea has high energy (high wind and high waves) . On the other hand DOR up to about 1:5 were found to be effective if the oil is viscous or emulsified and the sea condition has low energy so oil become very persistent on the sea surface and may contaminate the shore so increasing DOR permits these oil to be more rapidly dispersed and more readily biodegraded at sea.

All of these factors are important not only for efficient removal of floating surface oil but also for the conclusion biodegradation of the dispersed oil droplets.

5.6 The effectiveness of relevant dispersant for use under arctic and sub arctic conditions

Effectiveness of dispersant is defined as the percentage of oil that is dispersed into the water column following the application of dispersants.

P. J. Brandvik and his group [74] saw the effectiveness of some dispersants under arctic conditions and they defined arctic conditions as low temperature (0°C) and water salinities varying between 0.5% and 3.5%.

And from their study they found developed products designed for low salinity use are very effective at low salinities but suffer from a poor effectiveness at higher salinities. And they gave some recommendations:

- (1) It should be a new generation of dispersants with higher effectiveness over both a wider salinity range and at low temperature.
- (2) The physical properties for the dispersants should be relevant for low temperature operations. For example, high dispersants viscosity at low temperature may reduce the effectiveness due to the application difficulties.
- (3) Several logistic related subjects need further investigation before the potential of dispersants. For example, turbulence levels required for dispersion in ice and application systems for low temperature operations.

Corexit 9527 which contains surfactants in a water base is the only dispersant currently stock piled in Alaska and corexit 9500 which contains surfactant in a hydrocarbon base is a possible replacement for it.

There are three important factors in determining whether to use dispersants or not such as weathering states of oil (fresh, evaporatively weathered or emulsion), the salinity of the marine water and the temperature of the marine water [75]. These factors are known to modify the ability of dispersant to disperse the oil into the water column.

In sub arctic regions, most recent dispersants are formulated to have low viscosity at low temperatures, compensating any increase in viscosity of crude oils at subarctic temperatures [76]. Both Nes and Norland [77] and Byford [78] conclude that low temperatures have little effect on dispersant performance. In contrast Findas [11] found a two-fold rise in effectiveness of corexit 9527 in dispersing Alberta sweet crude oil with each three-fold rise in

temperature. Low temperatures may not affect dispersant but do affect the behaviour of the oil and thus the final effectiveness particularly for oil like ANS that is heavy and viscous.

Ross [76] has argued that the slight decline (32 to 22‰) in salinities in the Gulf of Alaska during the summer months is not of sufficient duration to alter dispersant performance considerably. Blondina [75] determined the effects of salinity on the effectiveness of corexit 9527 and corexit 9500 on fresh Alaska North Slope crude oil at 22°C. Both studies found little difference of dispersant performance at salinities between 22‰ and 32‰ at 22°C.

5.7 How to Maximize Dispersant Effectiveness

- Responding to the spill as quickly as possible while the oil is unemulsified and relatively small in area and large in thickness.
- Targeting only the thick portions of the spills and dosing these continuously until the proper dosage is achieved and the oil is dispersed.
- Using emulsion breakers or demulsifiers are often added to produce crude oils in low concentration to prevent emulsion formation or to "break" already-formed emulsions. In the spill control business there are many benefits of using emulsion breakers. Research has shown that:
 - (a) Demulsifiers can be sprayed onto oil spills in low concentration to prevent emulsion formation and even to break weakly-formed emulsions
 - (b) Certain demulsifiers are of very low toxicity.
 - (c) Certain demulsifiers are highly oleophilic, meaning that they will tend to stick to oil slicks once applied and not leach into the water column, so spills will be less persistent and will disperse naturally much more quickly, and spills will be more susceptible to chemical dispersion.
- In ice-infested water which has low energy conditions and this is will be a challenge for effective use of dispersants, using vessels to create artificial turbulence by propellers to initiate the dispersion rate is the solution for this problem [77].

6 THE TOXICITY OF OIL SPILL DISPERSANTS

Since 1960s, the research on the aquatic toxicology of oil spill dispersants started to be considerable because there was many major oil spills but the first generation of dispersant was more toxic because it contains some aromatics compounds in the solvents the type and aromatic content of the solvent being the main factors influencing the toxicity such as those used in the torry canyon spill. [79, 80] But products available today (second generation) are very low in toxicity –an order of magnitude lower than many common household products which could be related to loss of aromatic compounds from solution such as using nonanionic surfactant and solvents such as the glycol ethers[81] and water. .

6.1 Some factors influencing aquatic toxicity thresholds of dispersants or their component surfactants

Physicochemical [82]

- (1) Chemical composition
 - (a) Surfactants, molecular structure and ionic state
 - (b) Solvent, type and aromatic content
- (2) Condition of dispersant in water
 - (a) Chemical stability of dispersant and age of test solution
 - (b) Concentration and duration
 - (c) Properties of the water ,such as temperature ,salinity and oxygen

Biological characteristics of exposed organisms

- (1) Phylogeny (species)-wide range of sensitivities, such as comparisons of fish, bivalves, and crustaceans[83]
- (2) Life history-age and stage of development ,such as comparisons of eggs ,embryos, and larvae[84]
- (3) Physiology
 - (a)Condition-health and feeding state [80]
 - (b) Previous exposure and acclimation [85]
 - (c) Seasonal variation in sensitivity [86]

An understanding of these factors is important for the toxicity test and if we take for example the water temperature as a factor, corexit 9527 as a dispersant and artemia is the organism we can see if the water temperature was 25°C the LC₅₀ after one day will be 51-96 mg/L and if the temperature is 15°C the LC₅₀ will be ≥ 560 mg/L the difference between them will be 10^1 [87] and if we take another example the stage of development as a factor, BP1100 as a dispersant ,and the organism will be cod . After four days EC₅₀ < 1 (development from egg) and after four days EC₅₀ > 1000 (development from 9-day embryo) the difference between them will be 10^3 [88] so from the two examples we can see the quantitative influence between the different factors on toxicity thresholds of dispersants

6.2 Acute toxicity and sublethal toxicities of dispersants

There are many different kinds of dispersants, but I am interested in corexit 9527 and the other corexit series dispersants because of its effectiveness against fresh and weathered crude at low temperature [89]

The acute aquatic toxicity of Corexit 9527 was reported to be not much different from that of Corexit 9500 and Corexit 9554 [90]

Corexit 9527 was developed in 1972 for use on open sea oil slicks. Not Designed for Direct Application to Shorelines, Corexit 9580 Beach Cleaner Developed for That Application. Corexit 9527 is constitute of about 48% non-ionic surfactants, including ethoxylated sorbitan mono- and trioleates (Tween 80 and Tween 85) and sorbitan monooleate (Span 80), about 35% anionic surfactants, including sodium dioctyl sulfosuccinate (AOT), and about 17% ethylene glycol monobutyl ether as a solvent [91]. Corexit 9527 has harmful effects on marine species and shoreline species for example shoreline species such as Mallards (ducklings) when the concentration is greater than 150 mg/L the enzyme activity will increase in plasma but the lower level had no significant effect on enzymes [92] and example for marine species.

There have been reports of both negative and positive effects of Corexit 9527 on bacterial degradation of crude oil [93-95]. The explanations given for the effect of this surfactant mixture vary from a negative effect on the hydrocarbon uptake rate to a positive effect due to increased surface area of the substrate [96]. Per Bruheim [97] showed a detailed study which examine the interaction of the surfactants with bacterial cells, (*Acinetobacter calcoaceticus* ATCC 31012) was used and the result from this study was Corexit 9527 decreased the rate of oxidation of alkanes in crude oil by *A. calcoaceticus* ATCC 31012 rather strongly.

On the other hand, sorbitan monooleate (Span 80, a Corexit 9527 constituent) increased the oxidation rate very markedly. Tween 85 and Tween 80, the two other surfactant components of Corexit 9527, did not affect and slightly increased the oil oxidation rate, respectively. AOT, the prominent anionic surfactant constituent of Corexit 9527, had a very strong negative effect on the oil oxidation rate. The combination of Span 80 and AOT increased the oxidation rate, but not as much as Span 80 alone increased it. The correlation between Corexit 9527 and the mixture containing Span 80 and AOT was not quantitatively confirmed, but this may have been due to differences in surfactant concentrations and the presence of

Tween 80, Tween 85, and other anionic surfactants in Corexit 9527. Corexit 9527, ethylene glycol monobutyl ether, had no effect on the oxidation rate.

Acute toxicity increased with decreasing ethoxylate chain length, for example if ethoxylate chain is less than 6, LC₅₀ will be (1.3-3.29) mg/L and if the ethoxylate chain between (9-10), LC₅₀ will be (4.6-12.0) mg/L [98]. The sublethal effects in general for dispersants have harmful effects on the biological processes such as (growth, reproduction and development, behaviour and pathology growth). Some reproductive and physiological responses occur at levels below 100 mg/L after short exposures (10 to 40 min), but many of the sublethal responses have been observed only at high concentrations. And if someone takes a Corexit 9527 as an example if the threshold concentrations < 1 mg/L and the exposure time 20-40 min. A significant adverse effect on the fertilizing capability on sea urchin will occur [99].

Another example a Corexit 7664, if the threshold concentrations 10^3 - 10^4 and the exposure time >2 weeks, a disrupted embryonic development will occur on fish [100]

6.3 Sites and physiology of toxic action

Dispersants act, often on the respiratory organs and other tissues of aquatic organisms, depending on exposure time, on their nervous system and I will mention some sites and physiology of toxic action of surfactants and dispersants for some marine organisms

Effect on respiratory organs

- (1) Extreme physical damage to gills from anionic or nonanionic surfactant [101].
- (2) Change in gill and membrane permeability from anionic or nonanionic surfactant [102].
- (3) Respiratory rate increased, and then decreased from anionic and nonanionic surfactant [103].
- (4) Increased coughing rate from dispersants [104].

Effects on other tissues

- (1) Tissue swelling from anionic or nonanionic surfactant [105].
- (2) Changes in cell ultra structure from dispersant [99].

Effects on nervous system [106]

- (1) Temporary general blocking in activity from anionic or nonanionic surfactant.
- (2) Change in mobility from anionic and nonanionic surfactant and dispersant.

Other effects

- (1) Lipid metabolism changed from dispersant [107].
- (2) Complexion of proteins from anionic and nonanionic surfactant [108].

6.4 Chemical dispersants appear to protect organisms in some studies

In some studies chemically dispersed oil caused less environmental damage even, in shoreline releases compared with the adverse effect of untreated oil and this may be related to the adhesion of untreated oil to other surfaces.

For example *pacific herring larval abnormalities*, Pearson and his groups [109] had shown that chemically dispersed Prudhoe bay crude oil droplets adhere less to pacific herring eggs than did dispersed oil droplets and when the droplets adhered to the larval eggs they increase larval abnormalities but dispersed oil reduce the adverse effect of adhesion to larval eggs. Hence reduced adhesion should also reduce the adverse effects of oil on sea birds and marine mammal's, because dispersing the oil slick [110]

- (1) Can prevent or reduce the amount of oil enter the habitats.
- (2) Can prevent or reduce contamination because dispersed oil is less to adhere to the birds.

7 DISPERSANT SPRAYING EQUIPMENT

7.1 Equipment for dispersants should have some important functions such as:

- (1) Ability to operate under the existing environmental conditions and with available manpower and transport support.
- (2) Ability to deliver the correct chemical dosage to oil/water surface in a reliable manner.
- (3) Ability to provide mixing energy where required by the dispersant being used [111].

The following sections describe various types of equipment which have been demonstrated to control the required capabilities.

7.2 Vessel Dispersant Application Systems

Vessel systems are used for small and moderate near shore spills. There are three major types of vessel dispersant application systems [112].

- (1) Spray arm (spray boom) systems use overboard spray arms to apply diluted or undiluted (neat) dispersant.
- (2) Fire monitor systems apply dilute dispersant through systems designed to spray water or fire-fighting foam, and uses one of two possible chemical delivery systems (eductors or positive pressure chemical injection pump units).
- (3) Single nozzle undiluted dispersant application systems, are like fire monitors except that they are designed solely to apply undiluted dispersant. This newer concept is available in either a high pressure-low flow or low pressure-high flow operating condition.

The next section will be about each one in detailed:

(1) Spray Arm Systems



Figure 7.1: Dispersant spray arm system [113]

Historically, the most common vessel dispersant application equipment has been spray arm systems, figure (7.1). Spray arm systems generally are consisted of a dispersant pump system supplying two outboard spray booms, one projecting from each side of the vessel.

These systems are not permanently installed on vessels; but, they are added when a suitable vessel is needed for dispersant operations. Spray arm equipment for vessels should be lightweight for easy transport and loading, rough and strong to withstand wave effect and

sudden boat motion. The equipment should be quickly and easily installed, and not require complication such as welded attachments. Spray arm systems should have features that allow variation, regulation, and measurement of dispersant flow and water flow (if dilution is used). Nozzles should produce a flat spray of small droplets, not a mist or fog striking the water in a line perpendicular to the direction of vessel travel [114]. Nozzles should be placed such that the distance above the water surface is minimized as much as possible. Spray arm systems offer a high degree of simple control of few crews are trained in spray boom operation, and fitting the dispersant application systems onto vessels during an incident can be done quickly and inexpensively. The most effective use of dispersant is neat dispersant application with a spray arm system. Vessels with spray arm systems must travel through the oil slick during dispersant application. And the result of this, the vessel bow wave may push the oil slick out of the reach of the spray at typical vessel speeds, but the effect of the bow wave can be minimized by placing the spray arms as far forward as possible on board the vessel [115]. Speed during dispersant application must not be reduced because a limited vessel speed results in limited meeting against the oil spills.

(2)Fire Monitor Systems



Figure 7. 2: Dispersant fire monitor system [113]

Vessel fire monitors can be functioned as effective dispersant application platforms provided that proper nozzles, pressures, flow rates, dispersant metering, and vessel operation practices are employed figure (7.2). There are two major classes of dispersant application systems used with fire monitors: positive pressure chemical injection and eductors. Both of these systems dilute dispersant with seawater to achieve dispersant concentrations (5-10%) in the water stream [116-118]. This system relies on external pressure and metering systems to deliver dispersant to a pressurized water stream. If using positive pressure injection for dispersant delivery, the system should be able to deliver up to 30 gallons per minute (gpm) (114 litres per minute [Lpm]) of dispersant [119]. The second system uses eductors to educt water-soluble dispersant into a moving water stream at an adjustable rate this system does not require additional agitation since this is supplied by the water stream. The main advantage of eductors over positive pressure chemical injection pumps is mechanical simplicity.

According to AEA [120], the minimum fire monitors water pressure necessary for effective application of dispersant by fire monitor is ~ (3.5-4 bar). Although fire monitor use requires diluting dispersant in seawater potentially reducing the effectiveness of the dispersant at low

dispersant to oil ratio, fire monitors are capable of treating spilled oil quickly. Major and Chen [116] reported that a vessel with two monitors is capable of treating three to four times as much area as spray arms systems. The ability to treat spills faster is primarily due to their greater swath width, faster vessel speed during application and vessel pitch and roll do not affect fire monitors. So fire monitors are better suited for dispersant application in rough weather conditions. With a movable, operator-controlled nozzle, fire monitors also allow for directed spraying over heavy oiled areas. Additionally, surface vessels with fire monitors suitable for dispersant application are widely distributed in many ports and at remote oil drilling sites, allowing for rapid mobilization for dispersant application after an oil spill during the critical, early stages when dispersant application is most effective.

To ensure effective dispersant application, dispersant flow, water flow, water pressure before and after the eductor (if used), and at the nozzle outlet should be closely monitored [119].

(3)Single Nozzle Systems Designed for Dispersant Application

Single nozzle systems designed for dispersant application in undiluted form are a newer concept currently under development. Single nozzle systems would be simple to install, maintain, and operate, and allow for the dispersant spray to be directed to heavily oiled areas. In small oil spills, we need only a Small vessel arrangement of a single nozzle, high pressure-low flow system designed to deliver lesser quantities of dispersant. Single nozzle systems with a low pressure-high flow system are advantageous in that they allow for easily varying the output flow rate. Additionally, a different “fog” setting would allow operators to adjust droplet size to accommodate different dispersants or wind conditions. The ability to vary output flow rate and “fog” setting is advantageous where a highly variable surface slick exists [119].

7.3 Comparison of Vessel Application Equipment Systems

Table (7.1) summarizes the advantages and disadvantages of each vessel system when neat or dilute dispersant is used.

Table 7.1: Comparison of Vessel Application Equipment Systems [116, 120]

System: Spray Arm System, application of dilute dispersant	
Advantages	Disadvantages
<ul style="list-style-type: none"> • Simple dosage control and dispersant distribution • Uniform dosage/spray across swath width • Wide range of adjustment possible for vessel speed and dosage without changing nozzles 	<ul style="list-style-type: none"> • Heavy piping suspended over the side is more sensitive to sea state; complicated boom attachment/ship modification often required; boom contact with water on ship roll possible • Fine droplets easily blown off target due to wind • Potential decrease in dispersant effectiveness due to dilution prior to application at low dispersant-to-oil ratio (DOR) • Limited spray location control • Limited spray speed due to bow wave created by ship pushing oil slick out of the way • Lower treatment rate due to slower speed and small swath width • Requires installation on vessel • Not routinely available
System: Spray arm system, applications of neat dispersant	
Advantages	Disadvantages
<ul style="list-style-type: none"> • Uniform dosage/spray across swath width • Most effective use of dispersant • Typically fewer passes/number of systems needed than dilute application to effectively disperse oil • Can apply surface mixing after dispersant application 	<ul style="list-style-type: none"> • Heavy piping suspended over the side is sensitive to sea state; complicated boom attachment/ship modification often required; boom contact with water on ship roll possible • Fine droplets easily blown off target due to wind • Limited spray location control • Limited spray speed due to bow wave created by ship pushing oil slick out of the way • Lower treatment rate due to slower speed and small swath width • Requires installation on vessel • Not routinely available • Dispersant inventory can be rapidly exhausted

System: Fire Monitor System, application of dilute dispersant	
Advantages	Disadvantages
<ul style="list-style-type: none"> • A vessel with two monitors can cover up to three to four times the area of spray arm systems due to larger swath width and faster speeds • Droplets less sensitive to wind • Rugged enough to withstand permanent installation and better suited to rough weather/sea conditions • Can be permanently mounted without interfering with other operations • Can apply surface mixing after dispersant application • Widely available on larger vessels • Spray can be directed to heavily oiled areas by an operator 	<ul style="list-style-type: none"> • Variations in dosage across swath width can lead to uneven coverage resulting in limited oil encounter rate • Requires operator attention to generate the appropriate dispersant droplet sizes for effective mixing with oil slicks • Potential decrease in dispersant effectiveness due to dilution prior to application at low DOR • High water flow rates leads to high dispersant consumption, potential for wastage, and over application • Difficult to control dispersant dosage rates

System: Single Nozzle System, application of neat dispersant	
Advantages	Disadvantages
<ul style="list-style-type: none"> • Wider range of flow rates possible, with high flows easily achieved • Wider swath widths than multi-nozzle spray arm systems • Simple installation, maintenance, and operation relative to spray arm and fire monitor systems • Spray can be directed to heavily oiled areas by an operator • Can apply surface mixing after dispersant application 	<ul style="list-style-type: none"> • Variations in dosage across swath width can lead to uneven coverage resulting in limited oil encounter rate • Droplet sizes may need to be larger than droplets from spray arm systems in high wind situations • Little experience with field use (technology in development stages) • Dispersant inventory can be rapidly exhausted • Higher risk of over-dosing

7.4 The most important characteristics of vessels:

The characteristics of the vessels can be listed as following [121]:

- (1) Vessels should have enough supplies of dispersant, fuel, and crew facilities of work.
- (2) Vessels should be rapidly mobilized shortly after dispersant use approval.
- (3) Vessels should be located close enough to the spill place (typically less than 93 km) to arrive within the required time when dispersant use is effective.
- (4) Vessels should have large, open decks that allow access to the water surface.
- (5) Larger vessels (6-15 m in length) are required to allow for necessary personnel, equipment, and dispersant.
- (6) Vessels should be capable of high speeds (e.g, 18.5-28 km/hr) in order to transit quickly to oil spills and apply dispersant in the critical, early stages of the spill.
- (7) Vessels should perform well in rough seas.
- (8) Vessels should use single nozzle systems which are designed to provide a uniform spray pattern.
- (9) Vessels should have Pumps of sufficient size to deliver dispersant in dosages sufficient to treat slicks in the one millimetre thickness range in one pass.
- (10) Vessels should use concentrated dispersant without dilution in water because laboratory research proved that corexit 9500 is recommended to be used in neat form to eliminate the possibility of reduced effectiveness.

7.5 The operational procedure of dispersant application by vessels

A surveillance aircraft should be used to locate the oil slick and guide the spray ship. Again, good communications are essential. The ability to rapidly transfer IR images from the surveillance aircraft to the spraying ship by real time 'down-linking' is very useful. The speed of the ship during spraying should be between 4 and 8 knots. Care must be taken to avoid pushing the oil away with the bow wave caused by excessive ship speed. Break-up of the slick, caused by the spray ship or other ships sailing through it before dispersant spraying, should be avoided. Spraying into the wind is preferred; spraying with or across the wind may be necessary if the distribution of thick oil need this, but this may make spraying more difficult. Experience from field trials in Norway has shown that dispersant spraying with the wind can be successful. If cross-wind treatment has to undertaken, such as when the oil has formed narrow strips aligned across the wind, only the downwind spray arms should be used [122].

7.6 Advantages and disadvantages of Vessel Dispersant Application

The advantages of Vessel Dispersant Application:

- (1) Under some circumstances, vessel systems can provide a means of applying dispersant quickly and effectively in the critical hours and days following a spill.
- (2) Vessels offer certain advantages over aircraft systems in areas where vessels are present in abundance, including lower cost, ease of deployment, high degree of spray control and accuracy.
- (3) Vessels are alternative to aircraft for dispersant application for smaller, near shore spills.
- (4) Vessels can carry large amounts of dispersant and can remain spraying dispersants for long periods and in rough weather [120].

The disadvantages of Vessel Dispersant Application:

(1)The transit speed of ships is low and may not be able to reach the spill area until the “window of opportunity” for dispersant use has passed and this for areas very far from shore [120].

7.7 Aircraft dispersants application systems

It is good for remote areas, where very large slicks are involved or when sea conditions are too rough for dispersant application from vessels. There are two kinds of aircraft, helicopters and fixed- wing aircraft. There are some equipments suitable for helicopters for example, dispersant tank, motor-driven pump and spray units, all these equipment are suspended by sling from the helicopter, often referred to as “spray bucket”. This system has the advantages of not requiring any modification to the helicopter and can be used with different helicopters according to their availability. The carrying capability of the helicopter about (500 to 3000 L) of dispersant according to the model. The use of helicopters will be restricted to coastal zones or to areas near to the land but with distant oil spills it is important to install a field heliport with full support of dispersant at the closest point of the shore to minimize transit flight times [111].

In the other hand, there is some equipment adapted with the fixed-wing aircraft for example; the dispersant tank and pump are positioned in or under the central body of the aircraft and the spray units are fixed on the wings or the tail. There two kinds of the fixed-wing aircraft, single –engined aircraft and multi-engined aircraft. Single-engined aircraft used for dispersant spraying are small, designed for agriculture purposes and then converted for dispersant spraying. They have the ability to fly at low speeds (about 100 to 200 km/h) and at low altitudes (a few meters). But their capacity is limited (0.5 to 1.5 tonnes of dispersant). This restricts them to missions near the coast. As for and multi-engined aircraft, these are large with dispersant capacity (5 to 20 tonnes) and they are capable of carrying out missions at great distances from the coast (several hundreds kilometres) by more than one engine so this type of aircraft should be used only for large slicks. They need to fly at high speeds (200 to 400 km/h) and at higher latitudes (10 to 30 m), which can decrease the accuracy of the treatment. They also need an airport with a long runway (1,000 to 2,500 m) and supplies of dispersants and fuel. They have the ability of treating thick oil spill (about 1mm) [123].

7. 8 The operational procedure of dispersant application by aircraft

As in vessels spraying operations a surveillance aircraft generally locates the oil slick and then guides the spray aircraft (helicopter or fixed-wing) to the areas of thick oil and emulsion within the slick [124]. These areas may not be visible to the spray aircraft crew during

spraying because of the very low latitude, so good communication between the surveillance aircraft and the spraying aircraft is essential for accurate spraying. On instructions from the surveillance aircraft, the spray aircraft starts to spray dispersant, beginning from the edge of the area of thickest oil and flying into the wind, Figure (7.3).

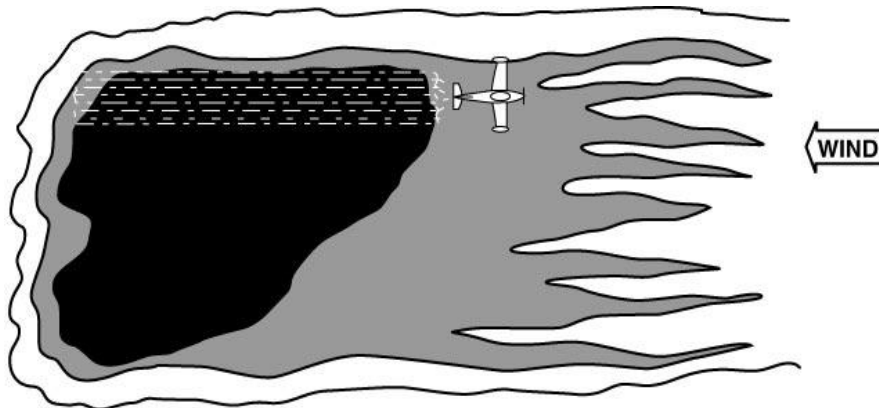


Figure 7.3: Aircraft spraying dispersant into the wind on a thick area of oil slick [124].

After the first spray run is completed, the spray aircraft returns to spray a gain next to the first one. Spraying is conducted as a series of continuous and parallel strips. Aerial spraying releases a long ‘cloud’ of dispersant into the air at the spray altitude. This dispersant ‘cloud’ settles under the influence of gravity and the wind. It is recommended that the spray aircraft fly directly into the wind so that the dispersant drifts directly back along the aircraft track and onto the area to be treated. Spraying across the wind may be necessary if the distribution of thick oil needs this, but it is much more difficult, Figure (7.4).

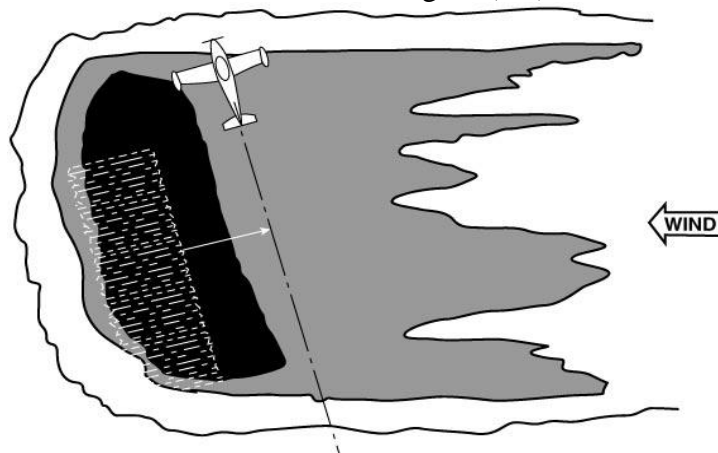


Figure 7.4: Aircraft spraying dispersant cross-wind on thick area of oil slick. [124]

7.9 Advantages and disadvantages of aircraft Dispersant Application

The advantages of aircraft Dispersant Application: [125]

- (1) Aircraft dispersant application is generally more effective than vessels in dealing with large or remote oil spills due to the ability of aircraft to reach and treat large areas in a short time period.
- (2) Aircraft can be used earlier during the spill incident

The disadvantages of aircraft Dispersant Application: [48]

- (1) The load carrying capacity of aircraft is limited, compared to large ships.
- (2) They need additional support facilities (e.g. airstrips and fuel).

(3) Larger aircraft have a greater load-carrying capacity, but are less manoeuvrable when dealing with scattered and broken-up oil patches that occur.

8 SHORELINE CLEANUP APPLICATION

Coastal environments are the most biologically productive of all marine areas [126, 127]. In addition, 78 percent of all world wide tanker spills occur within coastal waters [128, 129]. An understanding of the physical processes and shoreline characteristics influencing the distribution and effects of spilled oil is essential in planning appropriate mechanical or chemical cleanup operations.

8.1 The physical processes which are influencing oil distribution and persistence near-shore:

- (1) Wind stress and water currents.
- (2) Beach activity and grain size.
- (3) Tidal stage.
- (4) Wave energy.
- (5) Oil quantity and composition.
- (6) Ice effects.

(1) Wind stress and water currents

The movement of oil in water is controlled by winds and surface currents . An important example of this is during the Metula spill (9 August 1974, 260,000 tons deadweight grounded and ruptured its forward tanks while passing through the Strait of Magellan, Chile. Over the next four weeks, 51000 tons of Saudi Arabian crude oil and 2000 tons of bunkers C escaped to the surrounding waters. Spread by strong winds and tidal currents. Around 40000 tons of oil impacted about 250 Km of shoreline [130-133]. Biological damage was severe, killing 3000 to 4000 birds as well as mussels and nekton [134]. Strong westerly winds up to 100Km/h forced much of the oil on to the south eastern shore of the Strait of Magellan. Surface currents have the capability of moving oil at greater speeds than wind stress alone

(a 100-knot wind would move oil at only 3 knot). Currents may be caused by tidal action or alongshore drift. Changes in ●wind directions, velocity and duration, ●surface water currents and ●time of major oil release, all cause variation in the drift pattern of the spill.

(2) Beach activity and grain size

Beach activity refers to the erosional or depositional phase of shoreline development. Two types of activity are possible: The beach cycle which is a repetitive construction-destruction of the beach in response to waves and tides and the second one is erosion and deposition caused by alongshore sediment transport. Flat, long period waves generally move material onto the beach, while steeper, high-frequency waves (as during storms) do the opposite. Oil can be rapidly buried during the constructional stage in beach development, making cleanup more difficult. In addition to the beach cycle, oil may be buried by changes in beach morphology due to alongshore depositional-erosional patterns. Grain size influences the depth of oil burial and the thickness of oiled sediment, generally on coarse- grain beaches, the depth of oil burial and the thickness of oiled sediment increase. On fine-sand beaches, oil penetration was limited to the upper few centimetres [135].

(3) Tidal stage

Tidal stage is a major influence on the distribution and persistence of oil on the shoreline. For example, during the Metula spills, oil came ashore during spring high tides, forming thick oil layers along the highest portions of the beach. Oil deposited during the Metula spill and remained unaffected by wave activity for at least two years after the spill [136, 137]

(4) Wave energy

During and after oil impact, the action of waves on shoreline is an extremely influential process. For example, during the Metula spill, oil was quickly eliminated from zones exposed to direct wave attack. Most Chilean beaches showed oil remaining only on the highest and lowest portions of the beach, areas limited wave activity. In Chile both a march and a tidal flat received a large amount and long-lasting oil deposits. Two years later, these areas still appeared highly damaged. In summary, areas sheltered from wave action, including rocky coves, tidal flats and marches, received very heavy oil accumulations and show the greatest environmental damage. In contrast oil was held offshore by wave reflection and rarely came in direct contact with the shoreline [138].

(5) Oil quantity and composition

The quantity of oil spilled influences the shoreline. At low quantities oil is deposited primarily along the high-tide swashline. As the quantity increases; oil covers the rest of the beach face. Under heavy accumulations, the entire entire tidal zone becomes covered, for example in Metula spill; a massive spills have the capability of affecting large sections of coastline, 150 Km. Greater penetration and deeper burial occur with higher quantities.

The chemical properties of petroleum of petroleum vary among crude oils and processed oils. The boiling points, specific density and viscosity are the major factors influencing evaporation rates, solubility and dispersion [139]. Oils having a low boiling point will evaporate rapidly to the atmosphere and reducing the remaining volume of oil. Denser or more viscous oils such as Bunker C crude will evaporate and disperse much less. The viscosity of the oil also influences the penetration and the depth of the oil in the shoreline. Low –viscosity oil are able to penetrate deeper into the beach.

(6) Ice effects

Surface ice plays an important role in the dispersal of spilled oil. In general; the aerial extent of oil dispersal in environments covered with ice is orders of magnitude smaller than during open-water spills [140-142]. Oil may be trapped under the ice and when the ice melts or breaks up, much of the spilled oil will contaminate the unaffected areas. In general, oil is moved by tidal currents and accumulates in areas on the water's surface because of density differences. In addition significant, significant oil penetration may occur because of the high porosity of granular ice. For example ,the Buzzards Bay spill(happened on 28 January 1977,118 million litre of fuel oil ran aground in the north east section of Buzzards Bay). Ice acted to protect the beaches from oil contamination because the ice often acts as a natural barrier to spilled oil, and prevent contamination of the shoreline.

8.2 A classification of coastal environments

- (1) Exposed, steeply dipping or cliffed rocky headlands.
- (2) Eroding wave-cut platforms.
- (3) Flat fine sand beaches.
- (4) Steeper, medium-to coarse-grained beaches.
- (5) Exposed compacted tidal flats.
- (6) Mixed sand and gravel beaches.

- (7) Gravel beaches.
- (8) Sheltered rocky coasts.
- (9) Sheltered estuarine tidal flats.
- (10) Sheltered estuarine salt marshes and mangrove coasts.

A discussion and a photograph of each shoreline type are presented [143].

1-Exposed, steeply dipping or cliffed rocky headlands

The location of this one is in northern New England and along the pacific coast. Under high wave energy oncoming waves forcefully reflect back, and generating a return flow that prevents most oil from hitting the shoreline. So oil spill cleanup is usually unnecessary because of low level of contamination, figure (8.1).



Figure 8.1: Steeply Deeping [144]

2-Eroding wave-cut platforms

The location of this one in long island, southern New England, Cape Cod, and along the pacific coast . Wave action is also high, causing a rabid disappearance of spilled oil within weeks. In most cases, cleanup is not necessary, figure (8.2).



Figure 8. 2: Eroding wave-cut platforms [145]

3-Flat fine sand beaches

The location of this one in the south eastern Atlantic coast. Oil usually forms as a thin surface layer, due to the close packing of the sediment. Cleanup efforts should concentrate on removing oil from along the high-tide swash zone. In general the lower portions of the beach are rabidly cleaned of oil by natural wave action, figure (8.3).



Figure 8.3: Flat fine sand beaches [146]

4- Steeper, medium-to coarse-grained beaches

The location of this one in most coasts of the United States. Oil forms thick oiled-sediment layers and mixes deep into the beaches. Clean up is difficult without damaging the beach. Like before, Cleanup efforts should concentrate on removing oil from along the high-tide swash zone, figure (8.4).



Figure 8.4: Steeper, medium-to coarse-grained beaches [147].

5- Exposed compacted tidal flats

The location of this one in Bay of Fundy, Cape Cod bay, and Alaska. Oil does not penetrate into the compacted surface of these flats. Minor wave activity succeeds in pushing the oil across the flat and onto the beach. Actual oil deposition is small. Cleanup of the flats should be considered only if oil contamination is very heavy, figure (8.5).



Figure 8.5: Exposed compacted tidal flats [148]

6- Mixed sand and gravel beaches

The location of this one in New England, Nova Scotia and Alaska. Penetration and burial occur rapidly. The persistence of thick oil layers on mixed sand and gravel beaches in the strait of Magellan beach illustrates a long-term effect of oil in this environment, figure (8.6).



Figure 8.6: Mixed sand and gravel beaches [149]

7-Gravel beaches

The location of this one in New England, Nova Scotia and the Pacific North West. Oil is able to penetrate deeply into the coarse sediment of this type of beach. Under high wave energy conditions, oil can also be deeply buried under the gravel. Removal of all the oiled sediment during clean up, cause future erosion of the beach, figure (8.7).



Figure 8.7: Gravel beaches [150].

8-Sheltered rocky coasts

The location of this one in New England, Nova Scotia and parts of the pacific coast. The lack of wave activity permits oil to adhere to the rough surfaces of this environment. Biological damage is severe. Clean up operations may cause more damage than if the oil is left untreated, figure (8.8).



Figure 8. 8: Sheltered rocky coasts [151]

9-Sheltered estuarine tidal flats

The location of this one in the estuaries and lagoons of the Atlantic, pacific and gulf coasts. Biological life is large and may be subject to long –term damage by an oil spill. Removal of pollutant is impossible without causing further damage. But if the flat is very heavily oiled, cleanup should be done, figure (8.9).



Figure 8.9: Sheltered estuarine tidal flats [152]

10-Sheltered estuarine salt marshes and mangrove coasts

Salt marshes in the east coast of the United States, figure (8.10). Mangrove coasts in gulf coast of Florida, figure (8.11). Both of them are among the most biologically productive of all marine environments [153] Heavy oil contamination may cause long-term harmful effects. For example, two years after the Metula spill, a heavily oiled salt march on the south side of the Strait of Magellan showed almost no recovery. Oil may continue to exist in this area for ten or more years. Mangrove coasts affected by oil also show serious long-term effects [154, 155].



Figure 8.10: Salt marshes [156]



Figure 8.11: Mangrove [157]

So it is essential to understand the previously discussed physical processes and different shoreline environments in order to sufficient plane to cleanup by dispersants or mechanical means.

8.3 Cleanup methods

Many methods are available for removing oil from shorelines. All of them are costly and take a long time to carry out. I will discuss some of them [158-160].

1) Natural recovery: means leaving the environment to recover on its own. This option is suitable for small spills in sensitive environments and on a beach that will recover quickly on its own, such as non-persistent oils like diesel fuel on impermeable beaches.

2) Manual removal: is the most common method of shoreline cleanup. Teams of workers use gloves, rakes, forks, trowels, shovels, sorbent materials, hand bailers, or poles, to pick up oil, oiled sediments, and oily debris. Workers wear protective clothing such as splash suits, boots, gloves, and respirators if the oil is volatile. Material is connected directly into plastic bags, or buckets for transfer. It is a slow process but it generates less waste than other techniques. A disadvantage is the risk of injuries to personal from falls on slippery shorelines.

3) Flooding or washing shorelines: Is common cleanup methods. Low pressure less than about (50psi) washing with cool or mildly warm water less than about (30°C) causes little ecological damage and remove oil quickly. Warmer water removes more oil, but causes more damage. High pressure and temperature cause severe ecological damage and recovery may take years. Water can be applied to the beach by using hoses without nozzles to reduce the impact of the spray.

4) Vacuum systems: are useful for removing liquid oil that has pooled on beaches. The suction hose is usually applied manually to the oiled beach for collecting domestic waste.

5) Mechanical removal: By using tractors, front-end loaders, scrapers, road graders and excavators to remove the surface oil or oiled debris. Mechanical devices remove oil quickly from shorelines but also remove large amounts of other material and generate more waste than other techniques. Sand and sand gravel shorelines are best suited to this technique because they can support mechanical equipment and are not damaged by the removal of material.

6) Tilling and aeration: This work is done with farm equipment ,such as ploughs,discs,and cultivators and construction equipment such as bulldozers or graders with rippers to break up surface layers so the exposed oil can then weather naturally and degrade. The technique is suitable for sand and sand gravel shorelines.

7) Sediment reworking or surf washing: This work is done with graders, front-end loaders, or it can be done manually to move oiled material from the upper tidal zone, down to the intertidal zone where the oil will be washed out by the surf. The technique is suitable for sand and sand gravel shorelines.

8) Sorbents: Sorbents are left in place, on or near a beach, to absorb oil from the beach by natural processes and prevent it from decontaminating other beaches or contacting wildlife. Sorbent booms can be staked on the beach or in the water on the beach face to catch oil released naturally. This is effective but produces a large amount of waste material.

9) Beach cleaners or surface-washing agents: are chemical cleaning agents. These agents contain a surfactant and low-toxicity solvent. They insert molecules between the oil and the substrate so the adhesion of oil to the surface will be less and the oil will be dissolved. And then low pressure washing is used to move the oil to the water where it is recovered with skimmers. Before these agents can be used, approval from the appropriate environmental agencies is often required before these agents can be used.

10) Chemical dispersants: Dispersants generally increase the penetration of the oil, which makes them unsuitable for use on shorelines. But there is another opinion said that the application of dispersants is conducted on beaches, rocks, sea walls, and other shoreline structures during the final stages of cleanup after the bulk of stranded oil has been removed.

The most appropriate application equipment and technique depends on the shoreline substrate, ease of access and the scale of the operation. For small inaccessible beaches and coves, portable backpack sprayers are the most suitable. For large expanses of shoreline, purpose-built vehicles or tractors can be used [161].

In the 1980-1985 BIOS (Baffin Island Oil Spill) project, investigators wanted to determine whether or not it was wise to use dispersants on an oil slick approaching an arctic coastline. The results offered no convincing ecological reasons to prohibit use of dispersants in the near-shore environment [162]. According to Sergy ,“effective near- shore chemical dispersion will be preferable in many situations where shore line protection is of prime importance or where it is desirable to reduce the duration of exposure of subtidal benthos to oil. Likewise, it will most often be the preferred alternative to intensive shoreline cleanup”

Corals vary is sensitivity to oil pollution and are negatively affected by some dispersants [163- 165]. However, coral reefs in areas of small oil spillage have complete escaped damage [166]. In most cases, oil slicks will float over reefs without causing damage to the submerged corals and related organisms. Using dispersants close to the reef increase the exposure to oil, with possible damage to some of the organisms. So dispersants should not be used over or near coral reefs. But at the same time, there is a danger of oil slicks to reach on the upper parts of coral reefs during low tides. If this happen, it will be a serious damage to the reef organisms. So using dispersant spraying of the slick before it reaches the reef, as far a way from the reef as possible can minimize the damage [167].

9 OIL SPILL RESPONSE DECISION TREE AND CLEAN UP COST FACTORS

9.1 Decision-making at the time of the spill

When an oil spill occurs, time is very important particularly in regard to the use of dispersant. Agreement and prior approval for dispersant use are essential to facilitate a successful response. A recommended procedure for deciding whether dispersants should be used is shown in the following figure. If we look to the figure we can see the first step is to collect as much information as possible on the oil spill. This includes estimates of the size and location of the spill, the current and predicted weather/ wind conditions and characteristics of oil and this mean the type of oil and its properties.

After collecting information about the oil spill and this was the first step, the second step will be if sensitive resource like a shoreline is threatened or not. If there is no threat, surveillance of the oil should continue and there are many kinds of surveillance for example, Visual methods of surveillance are often the most practical and economical methods and these are best done from the air by a helicopter or aircraft using only the human vision but the disadvantages of this one if there is fog or darkness on which oil on the surface can not be seen, if the waves are high, it is difficult to detect the oil spill and very thin oil sheens are also difficult to detect specially in bad weathers . Remote sensing with various instruments such as infra-red/ultraviolet scanners is also a good kind of surveillance and has many advantages for example, using ultraviolet spectrum will be very useful for mapping out a very thin sheen and using infra red sensors give information about thicker slicks because thick oil on water absorbs infrared radiations from the sun and hence appears in infrared data as hot on a cold ocean surface. Remote sensing is usually carried out with instruments on aircraft or by satellite. But if there is a threat, all response options in the contingency plane should be considered according to some factors like size/location /weather/logistics.

Some times we need one option and some time we need more according to the best possibility of minimizing the environmental impact of the spill and the different areas of the slick may be handled with different response techniques. After we choose one or more options, we should consider the net environmental benefit analysis of each response technique. Based on the net environmental benefit analysis; one or more response options will be selected. For example, in an area where oil occurs above the coral reef and is moving quickly towards a mangrove. The use of dispersants could save the mangroves from severe damage but dispersing oil above the coral reef could cause some damage to the corals. Mechanical recovery could reduce damage, but there is not sufficient time to recover enough oil before contact with the mangroves occurs. A decision was made to use dispersant at once, to save the mangroves and then when more men and equipment are available, a mechanical recovery crew is sent to recover undispersed oil to prevent damage to mangroves, coral reef and oiling of shoreline. If approvals are needed like the previous example for use of dispersant or mechanical recovery, it must be obtained within hours. From the figure we can see four options, mechanical recovery, dispersant use, in- situ burning and allowing the oil to come ashore. If the last option is chosen, we should put on our mind how to protect the sensitive shoreline and how the shoreline will be cleaned. The expected effectiveness of each option should be determined, according to the available equipment, weather, conditions and logistics of the spill. Surveillance and monitoring of the effectiveness of the response options should be continued throughout the operation. If the effectiveness is not as expected, the spill response should be changed to ensure that money, time, and effort are not wasted [48, 167].

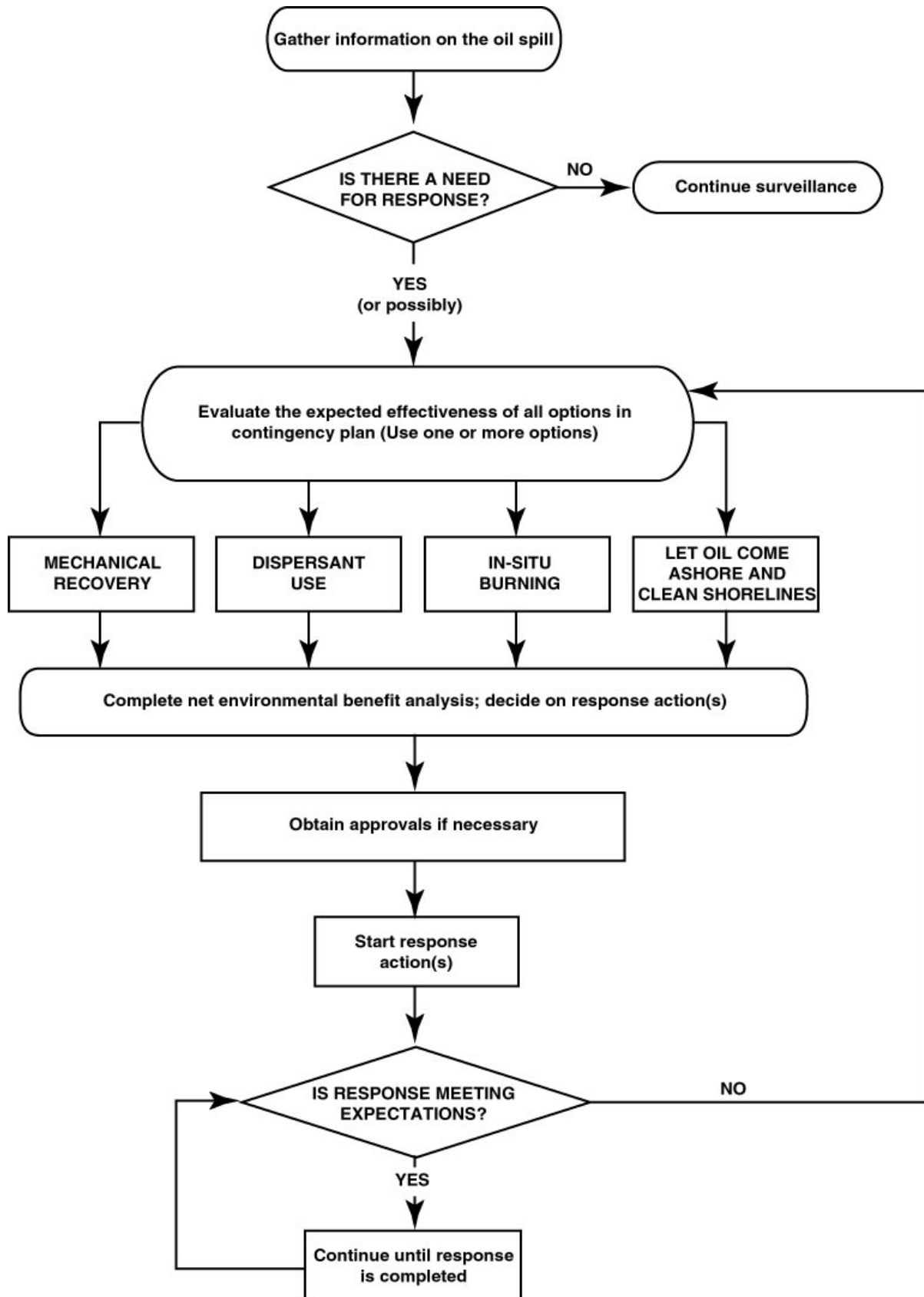


Figure 9.1: Oil spill response decision tree. [48]

9.2 Oil Spill Cleanup Cost Factors

There are many important factors which drive the costs, e.g. oil type, proximity to shoreline, location, cleanup methodology, and spill size. These factors can then be used to estimate costs for actual marine spills [168-170].

The impact of oil type on cost

The type of oil spilled impacts cleanup costs. Oil type determines the environmental impacts of the spill incident. Moller [171] found that cleanup costs for lighter crude and refined oils tended to be below the average spill cleanup cost.

The difference between diesel fuel oil spill and a heavy crude spill in terms of impact and the cleanup scenario are significant. Diesel fuel and light crude oil spills are significantly less expensive to clean up than spills of heavy crude or heavier fuel oil, which are more persistent. and the reason for that because Diesel fuel and light crude oil evaporate and dissolve very quickly after hitting the water surface.

Spills of more persistent products require more complicated cleanup strategies, which can include dispersant application when appropriate and when permitted by local statutes, or mechanical and manual recovery. Responses to spills of persistent oils that are near shorelines can result in long and difficult shoreline cleanup responses if offshore dispersant or mechanical containment and recovery operations are ineffective.

The impact of Shoreline Oiling on cost

The most expensive component of the oil spill cleanup response is the shoreline cleanup. This is generally the most labour-intensive and time-consuming part of the operation. Cleanup response strategists will use dispersant application, when appropriate and permitted by local regulations, and/or offshore mechanical containment and recovery operations to minimize shoreline oiling to reduce the impacts on the coastline.

It will be aggressive ecological impacts on the shoreline when we use hot-water washing or using of heavy machinery in our cleaning methods. In addition, such operations can cause greater long-term environmental damages.

So responses are moving towards gentler manual way, or towards “natural cleansing” options in shoreline locations that have exposure to intensive wave action [171].

The impact of location type on cost

Oil spill incidents were grouped according to their nearness to shore into “offshore”, “near shore (within 5 km of shoreline)”, and “in-port” location.

Oil spills that occur in near shore locations or in ports are significantly more expensive to clean up than offshore spills [172]. This is due to the higher probability for shoreline impact, particularly for persistent oils.

The impact of spill size on cost

An analysis of 96 oil spills [170] showed that cleanup cost/tonne was significantly negatively correlated with spill size. This correlation was also shown by Monnier [173]. Monnier found that spills of fewer than 10 tonnes had average per-unit cleanup costs of \$345,000/tonne, whereas spills of over 50 tons had costs of \$12,000/tonne. Smaller spills are more expensive to clean up than larger spills on a per-unit basis because of the costs associated with setting up the cleanup response, mobilizing the equipment and personnel, as well as bringing in the experts to evaluate the spill response and damages.

In the current study, spill responses for spills less than 30 tonnes were found to be more than ten times as expensive, on a per-unit basis, as for spills of 300 tonnes, Figure (9.2).

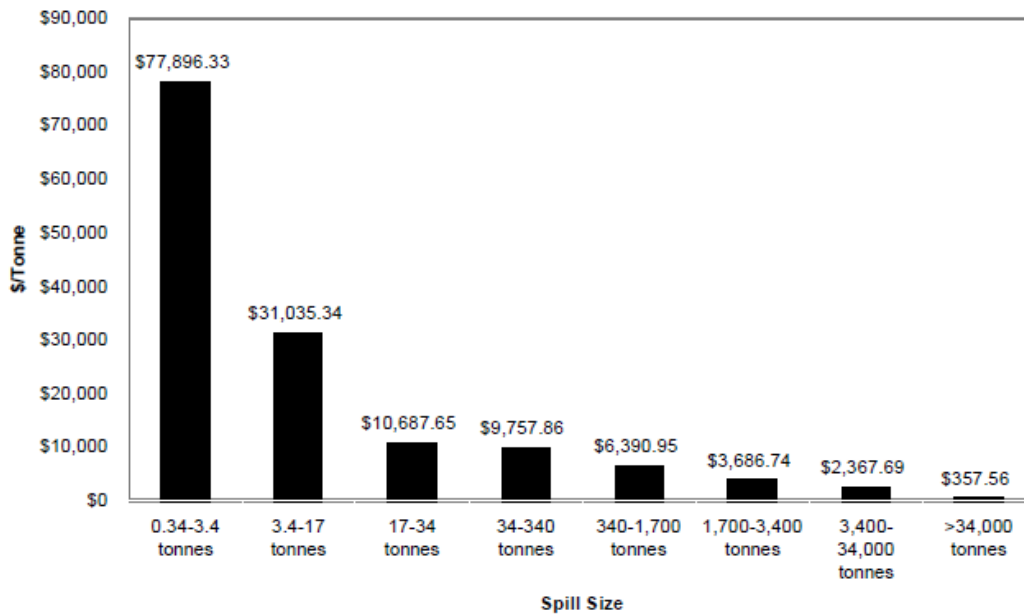


Figure 9.2: Per-Unit Marine Oil Spill Cleanup Costs for Non-US Spills [174]

The impact of location on cost

Perhaps the most important factor in determining the impact and response costs for an oil spill is the location. Sensitive locations can greatly impact its response costs. The political regime of the spill location can determine the standards of “how clean is clean?” options in non-mechanical/manual cleanup ways such as dispersants, labour costs, equipment costs, and response logistics.

The costs given represent only cleanup costs and do not reflect natural resource damage costs which may be caused in addition to cleanup costs depending on state, national, and international liability regulations.

Not surprisingly, the US ranks as one of the most expensive locations for spill cleanup responses. The high spiller liability, cleanup standards and labour costs of the US contribute to the higher cleanup response costs. Spills in Asia are relatively expensive. Much of this has to do with the need for high “how clean is clean” standards necessitated by the large aquaculture in the region.

In general, spills in more highly developed nations with high labour costs, complex regulations for spill response, and high standards for environmental protection rank as the most expensive, [175].

The impact of clean up strategy on cost

Cleanup strategy also plays a very large role in determining cleanup costs.

The use of dispersants in particular has been shown to significantly reduce the overall Cleanup costs [175]. The cost reduction can be attributed to the lower labour costs (fewer personnel for a shorter period of time) and even lower overall equipment costs that are required with dispersant application compared to mechanical containment and recovery operations. The lower labour costs are noticeable when manual cleanup compared to dispersant application.

In the analysis of cleanup costs from 97 spills in the oil spill intelligence report (OSIR), international oil spill database (OSIR database) [174]. This analysis showed that cleanup responses in which dispersants were the only or primary method were less expensive than spills involving other response measures, table (9.1).

Table 9.1: Oil spill cleanup cost comparison [175]

Cleanup Technique	Mean Cost/Tonne	Mean Cost/Liter
Dispersants only	\$2,184. 40/tonne	\$1. 96/liter
Dispersants Primary method	\$2,556. 98/tonne	\$2. 30/liter
Dispersant Secondary/tertiary method	\$14,233. 17/tonne	\$12. 79/liter
Other methods only (No dispersants)	\$12,802. 94/tonne	\$11. 51/liter

The reasons for the lower costs associated with cleanup responses centered on dispersant application are due to the reduction in shoreline impact, which reduces the need for expensive manual shoreline cleanup.

In-situ burning is another attractive option in terms of costs, but this option is not often used due to concerns over air pollution risks. Allen and Ferek [175] indicated that spill responses involving in-situ burning would cost on average \$162.29-\$402.34/tonne burned, as opposed to \$402.34-\$804.68/tonne per tone dispersed in responses using dispersants, and \$804.68 \$1,207.02/tonne per tonne mechanically recovered and disposed of. These calculations were based on theoretical cost estimates since there is little data on actual in-situ burning incidents. When the effectiveness of the various cleanup strategies is considered, table (9.2), the use of dispersants and even in-situ burning can be viewed as more cost-effective options [175]. The actual effectiveness of any cleanup methodology depends, of course, on the actual application methods, the individual circumstances of the spill (location, oil type, amount of oil), and unpredictable variables as weather.

Table 9.2: Reported Effectiveness of Cleanup Methodologies [176]

Method	Reported Field Effectiveness
Dispersants	80-90%
In-Situ Burning	90-98%
Mechanical Containment and Recovery	10-20%
Natural Cleansing	Up to 90% (under right conditions)
Manual Removal	Varies

10 OIL SPILL CONTINGENCY PLANNING AND DISPERSANT POLICY ISSUES IN NORWAY

10.1 Oil spill contingency planning in Norway

Oil spill contingency plans are developed to estimate the risk and to decide which response method (mechanical containment / recovery, dispersant use or possibly in-situ burning) is the most suitable way of dealing with potential oil spills [177]. In some circumstances it is possible to use qualitative criteria to decide between alternative responses approaches; if dispersant use is not effective because of the oil type or is not permitted by local regulations, mechanical recovery is the only realistic active option. In other cases, dispersant use may be the preferred option. Once the decision has been taken as to which response strategy is most appropriate, the amount of resources (equipment and personnel) that need to be deployed must be determined.

In Norway the oil companies operating off the coast of Norway are directed to develop contingency plans that meet specifications set by the Norwegian Pollution Control Authority (SFT). In the regulations of SFT state that the response alternative chosen should be the one that minimizes the environmental damage that would be caused by the oil spill, and this means all alternatives (chemical, mechanical and biological) should be evaluated regardless of cost, before selecting the most effective option. However, SFT also considers that response should also be based on cost-effectiveness. The oil companies must prove to the authorities that their choice of response, if it deviates from the minimum standards of mechanical recovery, is environmentally suitable for their particular operation.

The Oil Spill Contingency and Response (OSCAR) model system was developed by SINTEF [177].

The OSCAR system is designed to meet the following needs:

- establishment of objective, quantitative criteria for regulation and management purposes
- Oil spill training and Contingency planning
- support of oil spill response actions
- evaluation of alternative oil spill response strategies and logistics
- environmental risk and impact assessment
- environmental assessment of dispersant usage
- Cost-benefit analysis and optimisation for equipment purchase and disposition.
- net environmental benefit analysis

Key components in the system are shown in figure (10:1) and we can see from the figure SINTEF's oil weathering model [179-181], a three-dimensional oil trajectory and chemical fates model [182], an oil spill combat model [183-184], and exposure models for fish and ichthyoplankton [185-186], birds, and marine mammals [187]. The model calculates and records the distribution in three physical dimensions plus residence time of a contaminant on the water surface, along shorelines, in the water column, and in the sediments. The model is embedded within a graphical user interface in WINDOWS NT/95, which facilitates linkages to a variety of databases and tools. The latter allow the user to create or import wind time series, current fields, and grids of arbitrary spatial resolution. An oil and chemical database

supplies chemical and toxicological parameters required by the model. Results of model simulations are stored at discrete time-steps in computer files, which are then available as input to biological exposure models. I will explain some information about this model.

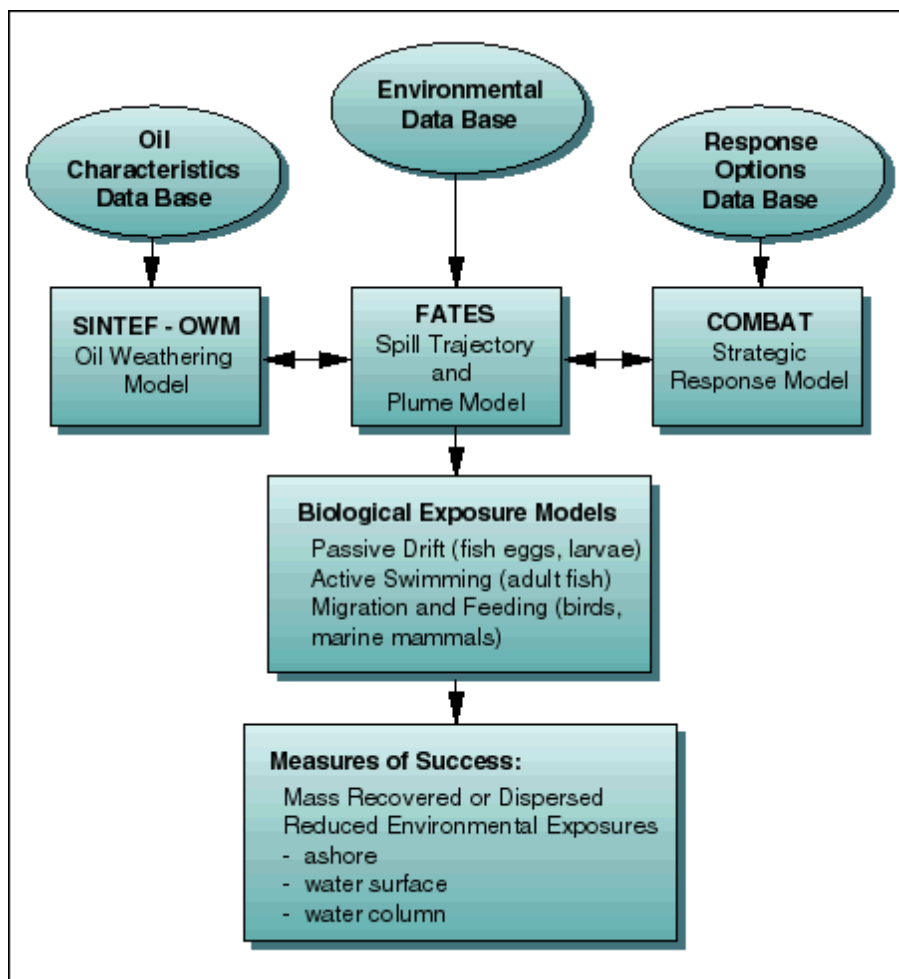


Figure 10.1: Schematic overview of the OSCAR system. [178]

Oil weathering data base

Oil and weathering data base supply chemical and toxicological parameters required by the model. An SINTEF oil spill weathering manual is the product of a thorough laboratory investigation coupled to a powerful computer model that predicts the changes in composition and behaviour of a crude oil that will occur if it is spilled at sea. The effectiveness of chemical and mechanical response methods are estimated. An SINTEF oil weathering model is a very powerful tool for effective oil spill contingency planning and will enable oil spill personnel to select the most appropriate response for a particular spill [25].

All SINTEF Oil Weathering Manuals are individually prepared for specific crude oil. The manual for particular oil will contain:

- A general section on the effects of composition on the behaviour of crude oils spilled at sea.
- Physio-chemical characterisation of the crude oil, residues that remain after evaporation of the light ends and emulsion that will be formed at sea.
- An assessment of the effectiveness of dispersants on the oil.

- Comprehensive predictions of the oil's behaviour at sea under different weather conditions.

Physical- chemical fates processes

The physical fate model estimates distribution of oil components on the water surface on shorelines, in the water column, and in sediment [25].

Spill response capabilities

Parameters for mechanical recovery and dispersant application system can be supplied by the user or taken from database. The recovery efficiency is dependent on wave height which in OSCAR is computed as a function of wind speed and water depth. Under ideal conditions a lot of oil can be recovered by boom but effectiveness is reduced as wave height increases. If infrared monitoring equipment is available, the user can continue the operation at night. OSCAR computes sunrise and sunset from latitude and longitude and calendar day [25].

10.2 Dispersant policy issues in Norway

Dispersant policy in Norway will be discussed as following: [75,188]

The Norwegian Pollution Control Authority (SFT) was established in 1974. It is a subordinate agency of the Ministry of the Environment and has responsibility for supervising the national emergency response system for acute oil pollution in Norway.

The responsibilities, and actions that should be taken when an oil spill occur is mainly ruled by the Pollution Control Act. Some central parts of this law are cited below:

- Anyone running an activity that can cause acute pollution is obliged to have sufficient means to prevent, notice, stop, remove and limit the impact of the spill. The level of contingency should be related to the probability of an accident, and also the consequences that can be expected.
- The authorities in charge of pollution can for activities that can cause acute pollution require a contingency plan to be made. Moreover, different parties can be ordered to cooperate over the required contingency. This means making a common plan of contingency and shares any equipment.
- Each of the municipalities is required to have a contingency to handle smaller cases of acute pollution in their own area. They are obliged to act when an acute incident happens and there is no private action taking place. The government is responsible for the contingency for larger cases of pollution that is not covered by municipal or private contingency plans.
- If acute pollution occurs, steps should be taken by the responsible party to avoid and limit the damage. In cases where this does not happen, the municipalities are responsible. They have to inform the SFT, which will assist if necessary. If the extent of pollution is great, the SFT can take full control of the operation.

On this basis there are three central actors in the Norwegian contingency against oil pollution: private actors, municipalities and the government through SFT. The oil companies are required to have their own contingency plans, and be able to deal with an incident. If they are not able to solve the situation, or the incident is caused by an activity that is not a part of the oil industry, the local municipality is responsible but If it is a major incident, SFT will provide support to the local action with equipment, vessels and personnel, or they will take control and run the response action.

The oil companies operating on the Norwegian continental shelf have formed an organization called Operating Companies Oil Spill Preparedness on the Norwegian Continental Shelf (NOFO). This organization provides equipment and trained personnel to act in an incident. It is required that each of the three parties provide assistance to any other if necessary. The primary objective is to contain and recover the oil as close to the source as possible. Every organization required to have a contingency plan for oil spills should consider dispersants to be an option.

International Agreements

The first international agreements concerning environmental protection of marine areas appeared around 1970. The increased marine activity made it clear that an incident at one site could easily affect several countries and their coastal lines. In the following part I will present the membership in international agreements for Norway that concern oil spills in Arctic areas.

▪Intervention Convention, 1969

International Convention Relating to Intervention on the High Seas in Cases of Oil Pollution

Its objective is to

- _ protect the interest of peoples against the dangerous consequences of maritime casualties resulting in danger of oil pollution of the sea and coastline.
- _ Recognize that measures of an exceptional character to protect such interests might be necessary on the high seas, provided these do not affect the principle of freedom of the high seas.

▪MARPOL 73/78

International Convention for the Protection of Pollution from Ships came into force, its aim is to:

- _ Eliminate marine pollution by oil and other harmful substances, and sewage and garbage.
- _ Minimize the amount of oil which could be released accidentally in collisions by ships, also including fixed or floating platforms.
- _ Improve further the prevention and control of marine pollution from ships, particularly oil-tankers.

▪OPRC, 1990

The International Convention on Oil Pollution, Preparedness, Response and Co-operation It aims to:

- _ prevent marine pollution incidents by oil, in accordance with the protection principle, in particular by strict application of the International Convention for Safety of Life at Sea (SOLAS) and MARPOL 73/78.
- _ putting in advance an adequate response in the event that an oil pollution incident does occur.
- _ providing co-operation between States for these aims.

▪Paris Convention, 1974

Convention for the Prevention of Marine Pollution from Land based Sources considers exchange of information and assistance in the prevention of accidents which might damage the marine environment.

▪ OSPAR Convention, 1992

Convention for the Protection of the Marine Environment of the North-East Atlantic. It replaces the Oslo and Paris Conventions, but decisions, recommendations and all other agreements adopted under those conventions will continue to be applicable.

The mission of OSPAR is to conserve marine ecosystems and protect human health in the North-East Atlantic by preventing and eliminating pollution; by protecting the marine environment from the adverse effects of human activities; and by contributing to the sustainable use of the seas.

Multilateral agreements

▪ Copenhagen Agreement

Agreement between Denmark, Finland, Iceland, Norway and Sweden on Information and Cooperation in Response to Pollution of the Sea by Oil or other Harmful Substances also covers aerial surveillance issues and cooperation in research and development.

▪ Trans-boundary Cooperation to Avert or Mitigate Disasters in Case of Accidents towards People, Property, or Environment, 1989

Agreement between Denmark, Finland, Norway, and Sweden. The agreement covers both preventing and limiting damage. It concerns cooperation in research and development as well as providing assistance in the event of accidents.

11 CONCLUSION

Today, oil spill responders try to optimize net environmental benefits when considering how to deal with a spill, and they try to choose the least distressful technique for a particular site, and balancing the advantages and disadvantages of each response, considering all relevant environmental conditions and implications and then comparing them to choose the best technique which optimize net environmental benefits.

In fact, the second generation of dispersants is very low in toxicity so, more than 75% of maritime nations allow dispersant use in oil spill response. Of those nations that allow dispersant use, over a quarter allow dispersant as a primary response option. Many nations prohibit the use of dispersants in near shore areas or near sensitive habitats, and use other products called beach or rock cleaners which are better adapted for such an application. However, in some countries, dispersants are also used for shoreline cleaning. A small percentage (less than 5%) of nations bans dispersant use outright. No single response option will be one hundred percent effective for all oils under all conditions, each has its limitations. But many other spills have demonstrated that dispersants are an important and potentially highly effective spill response tool, because it has many advantages such as dispersants can be used in stronger currents and greater sea states and ice like in arctic. It is the quickest response method. It protects the shoreline by removing the oil from the surface and stops the wind effect on the oil slick's movement. . It inhibits the formation of water-in-oil emulsions. It reduces the possibility of contamination of sea birds and mammals. It increases the surface area of oil that is available for natural degradation.

The recent oil spill which was happened in the Gulf of Mexico twenty of April 2010, they used more than 190,000gal of the dispersants, known as Corexit 9500 and Corexit EC9527A, to mitigate the damage from the oil spill and they think to inject dispersants at the site of the underground leaks but Federal agencies are evaluating potential environmental hazards of underwater use of dispersants before giving the green light to proceed further. And this is mean dispersants have many disadvantages such as, when the oil dispersed into the water column, it may affect some marine organisms which would not otherwise be reached by oil. It introduces an additional quantity of strange substances into the marine environment. There is a limited time window for dispersants. If used on shore it may increase the penetration of oil into the sediments.

In order to reduce the disadvantages of dispersants, improve dispersant science and the decision makers continue to apply this tool effectively and to the maximum environmental benefit, they must coordinate closely with scientists, planners, responders, government officials, and members of the public.

Appendix

It will be presented in appendix material safety data sheet of corexit ® EC9527A and this is the currently name of corexit 9527.



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

1. CHEMICAL PRODUCT AND COMPANY IDENTIFICATION

PRODUCT NAME : COREXIT® EC9527A
APPLICATION : OIL SPILL DISPERSANT
COMPANY IDENTIFICATION : Nalco Energy Services, L.P.
P.O. Box 87
Sugar Land, Texas
77487-0087
EMERGENCY TELEPHONE NUMBER(S) : (800) 424-9300 (24 Hours) CHEMTREC
NFPA 704M/HMIS RATING
HEALTH : 2 / 2 FLAMMABILITY : 2 / 2 INSTABILITY : 0 / 0 OTHER :
0 = Insignificant 1 = Slight 2 = Moderate 3 = High 4 = Extreme

2. COMPOSITION/INFORMATION ON INGREDIENTS

Our hazard evaluation has identified the following chemical substance(s) as hazardous. Consult Section 15 for the nature of the hazard(s).

Hazardous Substance(s)	CAS NO	% (w/w)
2-Butoxyethanol	111-76-2	30.0 - 60.0
Organic sulfonic acid salt	Proprietary	10.0 - 30.0
Propylene Glycol	57-55-6	1.0 - 5.0

3. HAZARDS IDENTIFICATION

EMERGENCY OVERVIEW

WARNING

Eye and skin irritant. Repeated or excessive exposure to butoxyethanol may cause injury to red blood cells (hemolysis), kidney or the liver. Combustible.
Do not get in eyes, on skin, on clothing. Do not take internally. Use with adequate ventilation. Wear suitable protective clothing. Keep container tightly closed. Flush affected area with water. Keep away from heat. Keep away from sources of ignition - No smoking.
May evolve oxides of carbon (COx) under fire conditions.

PRIMARY ROUTES OF EXPOSURE :
Eye, Skin

HUMAN HEALTH HAZARDS - ACUTE :

EYE CONTACT :
Can cause mild to moderate irritation.



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

SKIN CONTACT :

Can cause mild to moderate irritation.

INGESTION :

Not a likely route of exposure. Large quantities may cause kidney and liver damage.

INHALATION :

Not a likely route of exposure. Aerosols or product mist may irritate the upper respiratory tract.

SYMPTOMS OF EXPOSURE :

Acute :

Excessive exposure may cause central nervous system effects, nausea, vomiting, anesthetic or narcotic effects.

Chronic :

Repeated or excessive exposure to butoxyethanol may cause injury to red blood cells (hemolysis), kidney or the liver.

AGGRAVATION OF EXISTING CONDITIONS :

Skin contact may aggravate an existing dermatitis condition.

4. FIRST AID MEASURES

EYE CONTACT :

Flush affected area with water. If symptoms develop, seek medical advice.

SKIN CONTACT :

Flush affected area with water. If symptoms develop, seek medical advice.

INGESTION :

Do not induce vomiting without medical advice. If conscious, washout mouth and give water to drink. If symptoms develop, seek medical advice.

INHALATION :

Remove to fresh air, treat symptomatically. If symptoms develop, seek medical advice.

NOTE TO PHYSICIAN :

Based on the individual reactions of the patient, the physician's judgement should be used to control symptoms and clinical condition.

5. FIRE FIGHTING MEASURES

FLASH POINT : 163 °F / 72.7 °C (TCC)

EXTINGUISHING MEDIA :

This product would not be expected to burn unless all the water is boiled away. The remaining organics may be ignitable. Use extinguishing media appropriate for surrounding fire.

FIRE AND EXPLOSION HAZARD :

May evolve oxides of carbon (COx) under fire conditions.



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

SPECIAL PROTECTIVE EQUIPMENT FOR FIRE FIGHTING :

In case of fire, wear a full face positive-pressure self contained breathing apparatus and protective suit.

6. ACCIDENTAL RELEASE MEASURES

PERSONAL PRECAUTIONS :

Restrict access to area as appropriate until clean-up operations are complete. Stop or reduce any leaks if it is safe to do so. Do not touch spilled material. Ventilate spill area if possible. Use personal protective equipment recommended in Section 8 (Exposure Controls/Personal Protection).

METHODS FOR CLEANING UP :

SMALL SPILLS: Soak up spill with absorbent material. Place residues in a suitable, covered, properly labeled container. Wash affected area. LARGE SPILLS: Contain liquid using absorbent material, by digging trenches or by diking. Reclaim into recovery or salvage drums or tank truck for proper disposal. Contact an approved waste hauler for disposal of contaminated recovered material. Dispose of material in compliance with regulations indicated in Section 13 (Disposal Considerations).

ENVIRONMENTAL PRECAUTIONS :

Do not contaminate surface water.

7. HANDLING AND STORAGE

HANDLING :

Avoid eye and skin contact. Do not take internally. Ensure all containers are labelled. Keep the containers closed when not in use.

STORAGE CONDITIONS :

Store the containers tightly closed.

SUITABLE CONSTRUCTION MATERIAL :

PVC, Stainless Steel 316L, Hastelloy C-276, MDPE (medium density polyethylene), Nitrile, Plexiglass, Kalrez, EPDM, TFE, Alfax, Teflon, HDPE (high density polyethylene), Neoprene, Aluminum, Polypropylene, Polyethylene, Carbon Steel C1018, Stainless Steel 304, Compatibility with Plastic Materials can vary; we therefore recommend that compatibility is tested prior to use.

UNSUITABLE CONSTRUCTION MATERIAL :

Copper, Mild steel, Brass, Nylon, Buna-N, Natural rubber, Polyurethane, Hypalon, Viton, Ethylene propylene

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

OCCUPATIONAL EXPOSURE LIMITS :

Exposure guidelines have not been established for this product. Available exposure limits for the substance(s) are shown below.

ACGIH/TLV :

Substance(s)

2-Butoxyethanol

TWA: 20 ppm , 97 mg/m³



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

Propylene Glycol
OSHA/PEL :
Substance(s)

2-Butoxyethanol TWA: 25 ppm , 120 mg/m3 (Skin)

Propylene Glycol
AIHA/WEEL :
Substance(s)

For propylene glycol, an 8 hour TWA of 10 mg/m3 (aerosol) and 50 ppm (total).

ENGINEERING MEASURES :
General ventilation is recommended.

RESPIRATORY PROTECTION :
Where concentrations in air may exceed the limits given in this section, the use of a half face filter mask or air supplied breathing apparatus is recommended. A suitable filter material depends on the amount and type of chemicals being handled. Consider the use of filter type: Multi-contaminant cartridge (Gold) with a Particulate pre-filter (Purple). In event of emergency or planned entry into unknown concentrations a positive pressure, full-facepiece SCBA should be used. If respiratory protection is required, institute a complete respiratory protection program including selection, fit testing, training, maintenance and inspection.

HAND PROTECTION :
Neoprene gloves, Nitrile gloves, Butyl gloves, PVC gloves

SKIN PROTECTION :
Wear standard protective clothing.

EYE PROTECTION :
Wear chemical splash goggles.

HYGIENE RECOMMENDATIONS :
Keep an eye wash fountain available. Keep a safety shower available. If clothing is contaminated, remove clothing and thoroughly wash the affected area. Launder contaminated clothing before reuse.

HUMAN EXPOSURE CHARACTERIZATION :
Based on our recommended product application and personal protective equipment, the potential human exposure is: Low

9. PHYSICAL AND CHEMICAL PROPERTIES

PHYSICAL STATE	Liquid
APPEARANCE	Clear Amber
ODOR	Mild
SPECIFIC GRAVITY	0.98 - 1.02
DENSITY	8.2 - 8.5 lb/gal



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

SOLUBILITY IN WATER	Complete
pH (100 %)	6.1
VISCOSITY	160 cst @ 32 °F / 0 °C
POUR POINT	< -40 °F / < -40 °C
BOILING POINT	340 °F / 171 °C
VAPOR PRESSURE	< 5 mm Hg @ 100 °F / 38 °C Same as water
EVAPORATION RATE	0.1

Note: These physical properties are typical values for this product and are subject to change.

10. STABILITY AND REACTIVITY

STABILITY :

Stable under normal conditions.

HAZARDOUS POLYMERIZATION :

Hazardous polymerization will not occur.

CONDITIONS TO AVOID :

Freezing temperatures.

MATERIALS TO AVOID :

None known

HAZARDOUS DECOMPOSITION PRODUCTS :

Under fire conditions: Oxides of carbon

11. TOXICOLOGICAL INFORMATION

No toxicity studies have been conducted on this product.

SENSITIZATION :

This product is not expected to be a sensitizer.

CARCINOGENICITY :

None of the substances in this product are listed as carcinogens by the International Agency for Research on Cancer (IARC), the National Toxicology Program (NTP) or the American Conference of Governmental Industrial Hygienists (ACGIH).

HUMAN HAZARD CHARACTERIZATION :

Based on our hazard characterization, the potential human hazard is: High

12. ECOLOGICAL INFORMATION

ECOTOXICOLOGICAL EFFECTS :

No toxicity studies have been conducted on this product.



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

ACUTE FISH RESULTS :

Species	Exposure	LC50	Test Descriptor
Turbot	96 hrs	50 mg/l	

Rating :

MOBILITY :

The environmental fate was estimated using a level III fugacity model embedded in the EPI (estimation program interface) Suite TM , provided by the US EPA. The model assumes a steady state condition between the total input and output. The level III model does not require equilibrium between the defined media. The information provided is intended to give the user a general estimate of the environmental fate of this product under the defined conditions of the models. If released into the environment this material is expected to distribute to the air, water and soil/sediment in the approximate respective percentages;

Air	Water	Soil/Sediment
<5%	10 - 30%	70 - 90%

The portion in water is expected to be soluble or dispersible.

BIOACCUMULATION POTENTIAL

Component substances have a low potential to bioconcentrate.

ENVIRONMENTAL HAZARD AND EXPOSURE CHARACTERIZATION

Based on our hazard characterization, the potential environmental hazard is: Moderate

Based on our recommended product application and the product's characteristics, the potential environmental exposure is: Low

If released into the environment, see CERCLA/SUPERFUND in Section 15.

13. DISPOSAL CONSIDERATIONS

If this product becomes a waste, it is not a hazardous waste as defined by the Resource Conservation and Recovery Act (RCRA) 40 CFR 261, since it does not have the characteristics of Subpart C, nor is it listed under Subpart D.

As a non-hazardous waste, it is not subject to federal regulation. Consult state or local regulation for any additional handling, treatment or disposal requirements. For disposal, contact a properly licensed waste treatment, storage, disposal or recycling facility.

14. TRANSPORT INFORMATION

The information in this section is for reference only and should not take the place of a shipping paper (bill of lading) specific to an order. Please note that the proper Shipping Name / Hazard Class may vary by packaging, properties, and mode of transportation. Typical Proper Shipping Names for this product are as follows.

LAND TRANSPORT :

For Packages Less Than Or Equal To 119 Gallons:

Proper Shipping Name :

PRODUCT IS NOT REGULATED DURING
TRANSPORTATION



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

For Packages Greater Than 119 Gallons:

Proper Shipping Name :	COMBUSTIBLE LIQUID, N.O.S.
Technical Name(s) :	2-BUTOXYETHANOL
UN/ID No :	NA 1993
Hazard Class - Primary :	COMBUSTIBLE
Packing Group :	III

Flash Point :	72.7 °C / 163 °F
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AIR TRANSPORT (ICAO/IATA) :

Proper Shipping Name :	PRODUCT IS NOT REGULATED DURING TRANSPORTATION
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MARINE TRANSPORT (IMDG/IMO) :

Proper Shipping Name :	PRODUCT IS NOT REGULATED DURING TRANSPORTATION
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15. REGULATORY INFORMATION

NATIONAL REGULATIONS, USA :

OSHA HAZARD COMMUNICATION RULE, 29 CFR 1910.1200 :
Based on our hazard evaluation, none of the substances in this product are hazardous.

CERCLA/SUPERFUND, 40 CFR 117, 302 :
Notification of spills of this product is not required.

SARA/SUPERFUND AMENDMENTS AND REAUTHORIZATION ACT OF 1986 (TITLE III) - SECTIONS 302, 311, 312, AND 313 :

SECTION 302 - EXTREMELY HAZARDOUS SUBSTANCES (40 CFR 355) :
This product does not contain substances listed in Appendix A and B as an Extremely Hazardous Substance.

SECTIONS 311 AND 312 - MATERIAL SAFETY DATA SHEET REQUIREMENTS (40 CFR 370) :
Our hazard evaluation has found this product to be hazardous. The product should be reported under the following indicated EPA hazard categories:

X	Immediate (Acute) Health Hazard
X	Delayed (Chronic) Health Hazard
X	Fire Hazard
	Sudden Release of Pressure Hazard
	Reactive Hazard



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

Under SARA 311 and 312, the EPA has established threshold quantities for the reporting of hazardous chemicals. The current thresholds are: 500 pounds or the threshold planning quantity (TPQ), whichever is lower, for extreme hazardous substances and 10,000 pounds for all other hazardous chemicals.

SECTION 313 - LIST OF TOXIC CHEMICALS (40 CFR 372) :

This product contains the following substance(s), (with CAS # and % range) which appear(s) on the List of Toxic Chemicals

<u>Hazardous Substance(s)</u>	<u>CAS NO</u>	<u>% (w/w)</u>
Glycol Ethers		0.0 - 0.0

TOXIC SUBSTANCES CONTROL ACT (TSCA) :

The substances in this preparation are included on or exempted from the TSCA 8(b) Inventory (40 CFR 710)

FEDERAL WATER POLLUTION CONTROL ACT, CLEAN WATER ACT, 40 CFR 401.15 / formerly Sec. 307, 40 CFR 116.4 / formerly Sec. 311 :

None of the substances are specifically listed in the regulation.

CLEAN AIR ACT, Sec. 111 (40 CFR 60, Volatile Organic Compounds), Sec. 112 (40 CFR 61, Hazardous Air Pollutants), Sec. 602 (40 CFR 82, Class I and II Ozone Depleting Substances) :

This product contains the following substances listed in the regulation:

Substance(s)	Citations
<ul style="list-style-type: none">2-ButoxyethanolPropylene Glycol	Sec. 111

CALIFORNIA PROPOSITION 65 :

This product does not contain substances which require warning under California Proposition 65.

MICHIGAN CRITICAL MATERIALS :

None of the substances are specifically listed in the regulation.

STATE RIGHT TO KNOW LAWS :

The following substances are disclosed for compliance with State Right to Know Laws:

2-Butoxyethanol	111-76-2
Propylene Glycol	57-55-6

NATIONAL REGULATIONS, CANADA :

WORKPLACE HAZARDOUS MATERIALS INFORMATION SYSTEM (WHMIS) :

This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations (CPR) and the MSDS contains all the information required by the CPR.

WHMIS CLASSIFICATION :

D2B - Materials Causing Other Toxic Effects - Toxic Material



MATERIAL SAFETY DATA SHEET

PRODUCT

COREXIT® EC9527A

CANADIAN ENVIRONMENTAL PROTECTION ACT (CEPA) :

The substances in this preparation are listed on the Domestic Substances List (DSL), are exempt, or have been reported in accordance with the New Substances Notification Regulations.

16.	OTHER INFORMATION
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Due to our commitment to Product Stewardship, we have evaluated the human and environmental hazards and exposures of this product. Based on our recommended use of this product, we have characterized the product's general risk. This information should provide assistance for your own risk management practices. We have evaluated our product's risk as follows:

* The human risk is: Low

* The environmental risk is: Low

Any use inconsistent with our recommendations may affect the risk characterization. Our sales representative will assist you to determine if your product application is consistent with our recommendations. Together we can implement an appropriate risk management process.

This product material safety data sheet provides health and safety information. The product is to be used in applications consistent with our product literature. Individuals handling this product should be informed of the recommended safety precautions and should have access to this information. For any other uses, exposures should be evaluated so that appropriate handling practices and training programs can be established to insure safe workplace operations. Please consult your local sales representative for any further information.

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Annual Report on Carcinogens, National Toxicology Program, U.S. Department of Health and Human Services, Public Health Service.

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