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Oil spill problems and sustainable response strategies through new technologies

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Crude oil and petroleum products are widespread water and soil pollutants resulting from marine and terrestrial spillages. International statistics of oil spill sizes for all incidents indicate that the majority of oil spills are small (less than 7 tonnes). The major accidents that happen in the oil industry contribute only a small fraction of the total oil which enters the environment. However, the nature of accidental releases is that they highly pollute small areas and have the potential to devastate the biota locally. There are several routes by which oil can get back to humans from accidental spills e.g. through accumulation in fish and shellfish, through consumption of contaminated groundwater. Although advances have been made in the prevention of accidents, this does not apply in all countries, and by the random nature of oil spill events, total prevention is not feasible. Therefore, considerable world-wide effort has gone into strategies for minimising accidental spills and the design of new remedial technologies. This paper summarizes new knowledge as well as research and technology gaps essential for developing appropriate decision-making tools in actual spill scenarios. Since oil exploration is being driven into deeper waters and more remote, fragile environments, the risk of future accidents becomes much higher. The innovative safety and accident prevention approaches summarized in the paper are currently important for a range of stakeholders, including the oil industry, the scientific community and the public. Ultimately an integrated approach to prevention and remediation that accelerates an early-warning protocol in the event of a spill would get the most appropriate technology selected and implemented as early as possible – the first few hours after a spill are crucial to the outcome of the remedial effort. A particular focus is made on bioremediation as environmentally harmless, cost-effective and relatively inexpensive technology. Greater penetration into the remedial technologies market depends on harmonization of environment legislation and the application of modern laboratory techniques, e.g. ecogenomics, to improve the predictability of bioremediation.

Introduction

The Cambridge Energy Research Associates and Information Handling Services (CERA IHS) study in 2008 estimated that production from existing oilfields had declined over recent decades at 4.1–4.5% per year [1]. Such decline rates means that new production of ~ 9 million barrels per day has to be added just to maintain oil industry at current levels [2]. This would require novel field exploration and development technologies. Since oil production from newly explored or depleted reservoirs is more difficult, accidental oil spill risks increase. Generally, the production process, refining, storage and distribution are all potential sources of pollution of soil and water.

Currently almost a third of the oil consumed in the world comes from underwater reservoirs. Recent accidents on offshore oil platforms in Australia (Montara, 2009), United States (Deepwater Horizon, 2010), China (Penglai, 2011), Brazil (P-34 platform, 2012), and a North Sea gas platform (Elgin/Franklin, 2012) have raised public awareness of the extent to which offshore oil exploitation is moving into increasingly deep waters [3]. An empirical analysis of company-reported incidents on oil and gas platforms in the Gulf of Mexico between 1996 and 2010 indicated that incidents (such as blowouts and oil spills) correlate with deeper water. For an average platform, each 30 metres of added depth increases the incident probability by 8.5% [4].

Accidental spills at sea as a result of tanker or platform accidents are dramatic and high profile, but quantitatively represent less than 10% of total petroleum hydrocarbon discharges to the environment. Low-level routine releases represent as much as 90% of hydrocarbon discharges. In the marine environment it is estimated that about two million tonnes of oil enter the sea annually. However, only about 18% of this arises from refineries, offshore operations and tanker activities [5].

The spill location and magnitude often determine the strategy and technology applied for clean-up. Spills which happen at sea and coastal locations require different response actions than those on land. Spills on land are not usually as large and headline-capturing as those at sea although there are exceptions. It should be noted that the largest oil spill to date was deliberate [6].

In light of recent events, expected increase in demand for oil, and the risks involved in exploration in delicate and/or extreme environments, this review of oil spill prevention and remediation is timely. We wish to demonstrate that there is a need for further development of both "soft" technologies, such as contingency planning, and "hard" engineering solutions for spill prevention. Given the potential benefits of rapid, accurate decision-making immediately post-spill, the soft technologies can be very cost-effective in the event of failure of hard technologies.

We also wish to summarize the technologies for remediation and to increase awareness that a hierarchy of remedial technologies exists. Each spill is unique, so no single technology is fit-for-purpose. The environmental impact and sustainability of remedial technologies vary widely, but in an emergency, sustainability is not a top priority. Inevitably, a suite of remedial technologies is required, and this should be part of a decision support system – perhaps to be termed 'risk-based remedial design'. Bioremediation is often viewed with skepticism due to several unknowns.

However, it is necessary to emphasize its great importance even when not consciously deployed as a 'technology' as such.

The review also attempts to draw comparisons between marine and terrestrial spills (Table 1) because solutions might be fundamentally different. To these ends, the review is structured in two halves, treating response strategies in marine and terrestrial environments separately, which, it is hoped, adds to clarity of purpose.

A defining difference between marine and terrestrial spills is the speed at which oil moves or spreads and the resulting size of affected area [7]. Oil spilled on water is transported by wind and current, sometimes for long distances. Some oil evaporates (~5% by mass) and about 10% contributes to the surface slick, the same proportion dissolves or disperses within the water column, and almost one-third submerges in deep persistent plumes and accumulates on sediments [8]. Atmospheric and water conditions (e.g. temperature, wind, current, salinity, waves) can significantly increase oil transport and weathering rates. Consequently, the fate, behavior, and environmental effects of spills at sea are unpredictable and uncertain [9].

By contrast, oil spilled on land moves much more slowly and it usually flows downwards to accumulate in depressions. The movement speed is a function of the oil viscosity, air/ground temperatures, slope steepness, and surface conditions (roughness, soil permeability, vegetation) [7]. Since the prediction of transport pathways for oil on land can be more accurate, it is easier to design appropriate response strategy for terrestrial spills. However, the oil penetration into soil, its sorption by the soil matter, and physical and biological weathering are complex processes, which depend greatly on environmental conditions. For example, consequences of oil spillages in cold climate regions are more serious due to slow contaminant biodegradation at low temperatures and high vulnerability of Arctic and sub-Arctic ecosystems [10]. Spills occurring in marshes, springs and rivers can have even more serious consequences than those in soils.

Response strategies for marine oil spills

The principles of marine oil spill response are the prevention based on the "safety culture" and best response based on science and engineering [11]. The polluter now takes full responsibility for economic, social and environmental damage. So the safety culture has become a technological and political imperative for the maritime industry. Oil spill response is an extremely complex and challenging cross-disciplinary activity. In the decision-making process, it combines a wide range of issues and activities under emergency conditions that include: the nature of the material spilled, changes in physical and chemical properties (weathering) and biodegradation, local environmental conditions, sensitivity of impacted natural resources, and effectiveness of response/clean-up technologies [11].

Prevention strategies

Prevention of oil spills from marine platforms is addressed throughout the life cycle of exploration and production activities and is achieved by sound design, construction and operating practices, facility maintenance integrity, high levels of environmental awareness and staff training [12]. To mitigate possible spill scenarios and environmental risks, special measures are taken during the initial design phase. For example, oil pumps are engineered to prevent leakage and, as a fail-safe measure, they are equipped with shutdown devices that prevent spills if leakage does occur. Pumps are regularly tested to ensure that the seals prevent leakage, engines are overhauled to maintain integrity and operate shut-down systems properly. Corrosion-prevention techniques are employed, including metal design, cathodic protection, and corrosion inhibition chemicals.

Other spill prevention methods include spill collection facilities and blowout preventers [12]. The first are designed to direct spills from processing equipment into settling tanks where oil can be recovered, thus minimizing potential discharges to sea. To prevent blowouts, every well drilled should be fitted with a series of stacked blowout preventers, which immediately shut off oil and/or gas flow in emergency situations. There are three levels of well control, addressing drilling, operational and after blowout cycles [13]. The actual configuration varies widely depending on both the requirements of the operators and the regulators. This is becoming increasingly important as exploration goes into deeper, more hostile, waters. Failures of subsea blowout preventers have caused catastrophic accidents (Table 2) [14].

To ensure that petroleum products are transported safely and responsibly, a ship vetting system is applied [12]. Oil companies use this risk assessment process to ensure that the third party nominated oil tanker is a suitable vessel that meets necessary requirements to perform safe oil transporting. Specific vetting procedures vary from company to company, however key issues include a pre-selection questionnaire to determine the vessel suitability, searching on national or international databases to collect information on the vessel, such as: previous port inspections or vessel reports; incident and accident searches, and; final clearance inspections by pilots prior to permitting the vessel to enter a port or marine terminal. The vetting system acts as a decision-support and control mechanism to prevent high-risk vessels from entering a supply chain. Enhanced tanker vetting systems apply new internet-based technologies to automate and hasten decision processes [15].

Efficient responding to marine oil spills depends considerably on the preparedness of the organizations and persons involved in offshore oil production and transport. This can be enhanced by developing a contingency plan that outlines the steps that should be taken before, during, and after an emergency [16]. The International Convention on Oil Pollution Preparedness, Response and Co-operation (OPRC) recognizes the importance of contingency planning in timely and coordinated response to oil spills, which helps to minimize potential danger to human health and the environment. Integrated local, state, regional, and national contingency plans can assist response personnel to contain and clean up oil spills by providing information that the response teams will need when spills occur. Developing and exercising the plan provides the opportunity to identify roles and responsibilities, and to define best response strategies and operational procedures without the intense pressure at the spill time [17].

Windows-of-opportunity technology

Over time, contingency planning and spill response have been integrated to strengthen response capabilities. Each oil spill provides an opportunity to learn how to prepare better for future incidents. The critical elements that are often missing in oil spill contingency planning and best response are (1) an understanding of oil properties; (2) changes in these properties (weathering) over time; and (3) subsequent influence of these properties on technology effectiveness (Fig. 1) [18]. The technology windows-of-opportunity is an approach where science and engineering data and information are integrated to provide a scientific foundation for rapid decision-making in oil spill planning and response, and to optimize environmental and cost benefits by the selection of different oil spill response technologies [19]. The concept utilizes the following datasets: (1) dynamic oil weathering data; (2) actual (real time) remote sensing and environmental data, and; (3) dynamic performance data of oil spill clean-up technologies (Fig. 2). Dynamic oil fate and effects models have been developed to predict changes in oil properties over time and have been used as a decision-making tool in actual spill scenarios [8, 20].

Increasingly, smart software-based tools are assuming a role in contingency planning. Effective emergency decision support systems (DSSs) for disaster responders can reduce losses due to environmental damage. They are software systems that also include management science and operational research tools.

With marine oil spills, the very earliest hours post-spill before serious oil weathering are critical, and the ability to make rapid, data-based decisions can significantly influence the success of the response. There are many questions to be answered. The key one is: how much oil has been released? Other, critically important questions are: where is it?; what type is it?; when (and how) was it released?; what type(s) of ecosystems are threatened?; what is the sea state, wind speed and direction?. Answers are essential for correct decision-making: knowing which questions to ask in advance saves time in an actual incident.

Mathematical tools used in decision support for emergency situations generally suffer from protracted computing times and poor response rates. Liao and co-authors [21] proposed to overcome these deficiencies using intelligent methods such as artificial neural networks (ANNs), which are being increasingly used in environmental applications. They laid out the theoretical framework for generalised emergency response DSSs. They have also built an integrated methodology [22, 23] for developing an oil spill emergency preparedness tool which incorporates three intelligent mathematical model systems – case-based reasoning (CBR), genetic algorithm (GA) and ANN.

Case-based reasoning (CBR) uses experiences from previously solved problems to infer the solution to a current problem. It is fit for difficult reasoning such as response management for emergency accidents. GA is based on simulated biological inheritance and evolution, and uses an iterative searching method to determine an optimized solution. By integrating the methods with ANN, they claim to have proven the feasibility of deploying a quick and accurate response and preparedness system for on-site decision-making for oil spill response. Actual field testing will be needed to demonstrate its practicality.

Synthetic aperture radar (SAR) deployed on satellites has become an important tool in oil spill monitoring because of its wide area coverage, day and night applicability and insensitivity to adverse weather [24], although wind and waves can be limiting [25]. A large challenge in detection of oil spills in SAR images is accurate discrimination between oil spills and false targets, often referred to as look-alikes [26], such as algal blooms. Also, SAR generally cannot discriminate thick (>100 μm) oil slicks from thin sheens (to 0.1 μm).

The capability has since been improved by visible satellite sensors. During the *Deepwater Horizon* incident, a particularly important development was the AVIRIS hyperspectral approach to quantify oil thickness, a previously unobtainable achievement [27]. The authors believe that rapid response products, such as the Ocean Imaging expert system and MODIS (effectively a sophisticated digital camera) satellite data were critical during the *Deepwater Horizon* incident for the timely response needed to support decision-making. They favour a "paradigm shift" in oil spill research to enable operational readiness prior to the next large oil spill, rather than attempting to develop solutions during a spill.

Specific clean-up methodologies and technologies

Four major categories of response (clean-up) technologies are available to date: (1) chemical treatment (dispersants, emulsion breakers); (2) *in-situ* burning; (3) mechanical recovery (booms, skimmers, oil-water separators, adsorbents; and (4) bioremediation [28]. An environmentally preferred and cost effective spill response may require a combination of clean-up technologies.

Chemical treatment (dispersants, emulsion breakers)

Chemical dispersants are becoming increasingly accepted as the best response method in some circumstances such as adverse weather conditions or deep water. It is often a better option to disperse oil at sea, or even near shore, rather than allowing it to contaminate important sensitive resources. Dispersants were used on the *Deepwater Horizon* oil spill in unprecedented amounts (1.84 million gallons in total), much of it at great depth rather than at the surface [29]. Many viewed this tactic (of using a dispersant usually used on surface slicks at depth) as a great success. Clearly there were very rapid rates of biodegradation of the finely dispersed oil in the deep water [30]. The smaller the droplet size (increased surface area) appears to be a critical factor affecting the rates of hydrocarbon biodegradation [31]. Some though have questioned whether the chemical dispersant or the way the oil was physically injected into the water resulted in the formation of fine droplets that remained buoyant and moved away from the wellhead [32]. Thus there is a need for further consideration and more experimental and modeling testing before general recommendations can be made regarding the use of chemical dispersants.

Dispersants have two main components, a surfactant and a solvent. When a dispersant is sprayed onto an oil slick, the interfacial tension between the oil and water is reduced, promoting the formation of finely dispersed oil droplets. There is evidence that the combination of emulsified oil and dispersant could be more toxic than the oil itself (e.g. [33-35]). Therefore, advances have been made with dispersant formulation to make them less toxic and more biodegradable. However, dispersants have little effect on very viscous, floating oils, as they tend to run off the oil into the water before the solvent can penetrate. Similarly, they are unsuitable for dealing with mousse. Even those oils which can be dispersed initially become resistant after a period of time as the viscosity increases as a result of evaporation and emulsification. The time window is unlikely to be more than a day or two. Dispersants can, however, be effective with viscous oils on shorelines because the contact time is prolonged, allowing better penetration of the dispersant into the oil.

The decision to use dispersant is multi-faceted: in the decision-making process are environmental issues such as sea state (often when booms and skimmers cannot be used in rough seas, then dispersants may be an option); oil issues relating to its composition and weathering; and dispersant-specific issues such as approval and availability [36]. Their future deployment in the Arctic should be dependent on the results of toxicity tests of chemically dispersed oil at realistic concentrations and exposures using representative Arctic species [37].

It is generally considered essential to recover as much released oil as possible from the marine environment. Therefore, emulsion breaking and oil recovery must be attempted at the earliest stage in the oil spill response [38]. The addition of demulsifiers at low concentrations can facilitate oil-water separation because they counter the effects of emulsifiers naturally present in oil [39]. Application of emulsion breakers to oil-water separators reduces the quantity of water collected, thereby improving oil collection efficiency [40]. However, effective use of emulsion breakers depends greatly on oil properties, environmental conditions, application methods and time after a spill [41].

In-situ burning

This is generally considered to be a technique of emergency. It has not routinely been employed in the marine environment. However, it has been considered as a primary spill response option for oil spills in ice-affected waters since offshore drilling began [42]. It is therefore considered a viable spill response countermeasure in the Arctic [37]. If the oil spill is in remote waters, and the options are few, *in-situ* burning can be an acceptable solution. Fire-resistant booms [43] are connected to vessels. The vessels sail though the oil spill, forming the boom into a U-shape, collecting oil in the boom being trailed behind. The vessels then sail to a safe distance from the spill and the oil is ignited. There are many safety checks required to guarantee the safety of the personnel involved, particularly regarding smoke inhalation.

If crude oil has weathered to form a water-containing mousse (around 30-50% water) which has lost most light fractions, then ignition is not easy. Efficiency of burning is highly variable and is largely a function of oil thickness. A slick of 2 mm burning down to 1 mm burns much less efficiently than a pool of oil 20 mm thick burning down to 1 mm. M.F. Fingas [44] described general conditions necessary for *in-situ* burning. A variety of igniters have been used; they range from highly specialized pieces of equipment to simple devices that can be manufactured on site from commonly available component parts [45]. Among the most sophisticated are the helitorch devices, which are helicopter-slung devices that dispense packets of burning, gelled fuel and produce a flame temperature of 800°C.

The decision to burn requires a balance of various consequences to be made: burning the oil eliminates the environmental impact of the oil slick, but converts most of the oil to carbon dioxide and water. Burning generates particulates and toxic gases, thereby creating air pollution. However, not burning the oil enables an oil slick to spread over a large area and impact the environment. The latter prevents particulate formation, but up to 50% of the oil can evaporate, causing air pollution in the form of volatile organic compounds (VOCs). A concise description of the advantages and disadvantages of burning is given in [46].

The smoke plume emitted by burning an oil slick on water is often the primary concern as low concentrations of smoke particles at ground or sea level can persist for a few kilometres downwind. In practice, smoke particulates and gases are quickly diluted to concentrations below levels of concern [47]. The potential cancer risk level and non-carcinogenic hazard index associated with exposure to poly-aromatic hydrocarbons (PAHs) in smoke from burning an oil spill is considered below levels of concern [42]. However, particulate concentrations can have acute respiratory effects. Therefore, Buist and co-authors [42] suggest that precautions may need to be taken to minimize such exposures if a burn is conducted 1000 to 2000 metres from a population center.

The residue remaining after burning is primarily composed of higher molecular weight compounds of oil with minimal lighter or more volatile fractions. According to [48], it exhibits little water or lipid solubility and has no detectable acutely toxic compounds. Aquatic toxicity tests performed with water after experimental burns also did not find any adverse effects. It is considered to pose less risk to marine mammals and birds and shorebirds than the unburned slick [42].

Compared to other response methods, *in-situ* burning can reduce the number of people required to clean beaches, and can reduce injuries associated with this hazardous work. By eliminating the oil at the source of spill, contact of oil with marine birds and mammals can be reduced. N. Barnea [49] described four case studies of *in-situ* burning, each representing a different scenario: on the open sea, in a river, in a wetland, and inside a stranded vessel. Each requires different decision-making considerations, but evidently *in-situ* burning can be an effective technique. It has been used in several high-profile oil spills e.g. *Exxon Valdez* [50]. During the *Deepwater Horizon* event, it was used extensively (411 burns) to remove 40-50 million litres of crude oil [27]. A detailed description is given in [51]. Yoshioka and co-authors [52] concluded that 10–20% of historical spills could have been candidates for *in-situ* burning.

Some of the current limitations of *in-situ* burning (hazards associated with smoke, the difficulty or impossibility of ignition of emulsified oil) have been tackled by Tuttle and co-authors [53]. They have demonstrated the use of a flow-blurring atomizer for producing a flammable aerosol of crude oil and emulsified crude oil. It required no additional air or fuel flows, and required low liquid and air pressures to produce a stable, flammable spray plume. Crucially, emissions from the plume included unburned oil with minimal smoke observed, when compared to *in-situ* pool fire flames.

Mechanical recovery (booms, skimmers, oil-water separators, adsorbents)

Booms would not be regarded as 'advanced' technologies; nevertheless they are at the vanguard of spill control. They are used for containment, i.e. they control the spread of oil to reduce the possibility of contamination of beaches and shoreline. They also concentrate the oil into thicker layers to make it easier to recover, or to ignite for *in-situ* burning. There are several types of booms: an above-water freeboard to contain the oil and to prevent waves splashing over the top; a flotation device; a below-water skirt to contain the oil and to minimize oil loss under the boom; a longitudinal support, such as a chain or cable to strengthen the boom against wave or wind action [54]. There are a large number of combinations of boom types and operating conditions for fast currents (e.g. open sea, coastal, estuary) and a useful training guide has been published by the US Coast Guard [55].

Most booms perform well on calm seas, but they perform poorly if waves are higher than 1-1.5 metres or the tide is faster than one knot per hour [38]. Under these conditions the separation efficiency diminishes due to water ingress over the boom or oil egress under it. Also, if either the towing speed of the boom or the amount of the confined oil, or both, exceeds certain critical values then confined oil will leak beneath the floating boom [56]. In rivers with fast currents, for example, boom containment is notoriously difficult. Conventional boom systems are limited to operational speeds of 0.7-1.0 knots. This requires recovery vessels extremely slowly, frequently straining the engine and transmission. New commercial systems, designed for rough conditions such as the North Sea, are available with design improvements to slow the surface water and oil significantly, which allows operation at up to 3 knots, and with wave heights up to 3 metres [57].

Another commercially available improvement is to combine collection and recovering spilled oil. Pulled by two towing vessels, an oil boom can gather oil in an oil sump at the rear, and a recovery pump can be inserted in the oil sump to recover the oil. The maximum towing speed is purported to be 5 knots [58].

As with booms, skimmers lose efficiency in rough water. Skimmers are either self-propelled devices or can be operated from vessels. Their function is to recover oil, rather than contain it [38]. Three types of skimmers are in common use: weir, oleophilic and suction [59]. All are rather simple in concept and design, and each offers advantages over the others. For example, weir skimmers are prone to being jammed or clogged by floating debris. Oleophilic skimmers have belts or continuous mop chains made of oleophilic materials which blot oil from the water surface, and work well in the presence of debris or ice. Suction skimmers work much like a vacuum cleaner, and are thus prone to clogging.

The separation of water from oil collected during oil recovery operations is a necessary requirement that determines the cost of oily water transport and storage, salvage value of separated oil, and labour costs associated with long-term recovery actions [40]. This includes the separation of oily droplets from the water (de-oiling) or draining emulsified water from a chocolate mousse type water-in-oil emulsion. In both cases, oil–water separation and adsorption devices are used. Oil spill recovery separators suitable for vessels-of-opportunity use include traditional gravity-type coalescing separators and centrifugal devices, e.g. hydrocyclones.

Sorbents are oleophilic materials that sorb oil and repel water. There are three classes of sorbents: organic (waste agricultural products), mineral (vermiculite, zeolites, activated carbon, organo-clays), and synthetic (polypropylene and polyurethane), differing in recyclability, wettability, density, geometry and sorption capacity [60]. A problem with sorbents is that their use can be labor and time consuming. An increase in oil and emulsion density over time will significantly reduce the buoyancy difference between the spilled product and seawater and subsequently reduce the buoyancy of sorbents. Moreover, changes in emulsion viscosity, resulting from oil evaporation and emulsification, interfere with sorbent effectiveness [28].

Bioremediation

Naturally occurring microorganisms, which are widely distributed in marine environments, have an enormous capacity to decompose petroleum hydrocarbons [61, 62]. Many different species of microorganisms have evolved the ability to catabolise petroleum hydrocarbons, which they use as sources of carbon and energy to make new microbial cells. Most of the tens of thousands of chemical compounds that make up crude oil can be attacked by bacterial populations indigenous to marine ecosystems. Some microorganisms degrade alkanes and other saturated hydrocarbons. Others degrade aromatic hydrocarbons. Some specialize in degrading higher molecular weight polycyclic aromatic hydrocarbons. Some degrade multiple classes of hydrocarbons. When petroleum enters the oceans, a consortium of different bacterial species rather than any single species acts together to break down the polluting complex mixture of hydrocarbons into carbon dioxide, water, and inactive residues (Fig. 3).

While in many cases biodegradation can mitigate toxic impacts of spilled oil without causing ecological harm, environmental conditions for it to happen rapidly are not always ideal [62]. In the case of major oil tanker spills and well blowouts the rates of natural hydrocarbon biodegradation are often too slow to prevent ecological damage. The rates of hydrocarbon biodegradation, though, can be accelerated in many cases so as to reduce the persistence times of hydrocarbon pollutants, a process known as bioremediation. For general overviews of petroleum biodegradation and bioremediation (see [63, 64]).

Because seawater is a poor source of the required nutrients nitrogen and phosphorus, bioremediation employing fertilizers to increase the concentrations of these nutrients needed for growth by hydrocarbon degrading microorganisms was used in the cleanup of shorelines impacted by the *Exxon Valdez* oil spill [65]. The use of fertilizer-enhanced bioremediation complemented the physical cleanup of oil and was applied to surface and sub-surface porous sediments (e.g., boulder/cobble/gravel shorelines). The *Exxon Valdez* spill was the first time a full-scale, microbial treatment process was developed using bioremediation. In all, 48,400 kg of nitrogen and 5,200 kg of phosphorus were applied from 1989–1991, involving 2,237 separate shoreline applications of fertilizer [66]. Monitoring showed a mean loss in the mass of residual oil of about 28% per year for surface oil and 12% per year for sub-surface oil.

The decision to employ bioremediation in the cleanup of shorelines in Prince William Sound that were oiled by the *Exxon Valdez* spill followed extensive laboratory and field tests. With extra nutrients and dissolved oxygen added to flasks, microbes degraded up to 90% of alkanes and about 36% of the initial total oil mass in 20–60 days. This represents a three-fold enhancement of the biodegradation rate compared to unfertilized controls [66, 67].

Field tests were conducted on test plots at oiled shorelines in Prince William Sound. The field tests examined three different types of fertilizers: (1) a water-soluble fertilizer, typical of what would be used in garden; (2) a solid, slow-release fertilizer that would gradually release nutrients (similar to that used on lawns): Customblen® 28-8-0, manufactured by Sierra Chemicals of California; and (3) an "oleophilic" liquid fertilizer, designed to adhere to oil: Inipol®, manufactured by Elf Aquitaine of France. These three fertilizers were chosen based on application strategies, logistical issues for large-scale application, commercial availability, and the ability to deliver nitrogen and phosphorus to surface and sub-surface microbial communities for sustained periods.

About two weeks after the oleophilic fertilizer was applied, there was a visible reduction in the amount of oil on rock surfaces [68, 69]. The treated areas even looked clean from the air, which was important for gaining public and political support; but it was not enough to meet scientific standards. Additional field testing confirmed that the rate of oil degradation under these conditions was critically dependent on the ratio of nitrogen to biodegradable oil [70]. Biodegradation rates for polycyclic aromatic hydrocarbons (PAH) could increase by a factor of two, and for aliphatic hydrocarbons by a factor of five, with fertilizer.

In addition to evaluating the benefit of adding fertilizer to stimulate the indigenous microorganisms (the approach that was actually employed for bioremediation) consideration was given to adding products containing hydrocarbon-degrading microorganisms. Exxon received several proposals claiming specific commercial bioremediation agents, including cultures of microorganisms, would be effective for cleanup. None of the products, however, had an established scientific basis for application to the shorelines of Alaska. Laboratory tests were conducted by the United States Environmental Protection Agency (EPA) on 10 technologies, and field tests were performed on two [71]. The tests failed to demonstrate that any of the products were effective. Given the failure of microbial seed agents to increase rates of oil biodegradation under real-world conditions, the EPA judged the use of such agents for treating oil spills as dubious [72].

Despite the very successful use of bioremediation on shorelines of Prince William Sound, Alaska, some oil from the *Exxon Valdez* spill remains sequestered in patches under boulder and cobble on a few shorelines. Venosa and co-authors [73] showed in laboratory experiments that if sediments were displaced, so that the oil was no longer sequestered, rapid biodegradation of the residual oil would occur. They concluded that oxygen is the main limiting factor. They also postulated that if nitrate was added there could be anaerobic biodegradation of associated organic matter so that the porosity of the sediments would increase and oxygenated water could reach the oil. Boufadel and co-authors [74-76] have proposed injecting nutrients and oxygen to stimulate biodegradation of the residual sub-surface oil. Atlas and Bragg [77] have contended that the value of any such treatment will likely be very limited. The debate, thus, continues about whether bioremediation can still be effective more than more than two decades after the spill.

Summarizing the major lessons learned from the *Exxon Valdez* spill [78]:

(1) Bioremediation can be an effective technology for oil spill cleanup. In the case of the *Exxon Valdez* spill, it was possible to speed up the rates of natural biodegradation by adding fertilizers to the surfaces of oiled shorelines. Accelerated rates of three to five times were achieved without any toxicity to biota or any other adverse environmental impacts;

(2) Efficacy and safety of bioremediation must be scientifically demonstrated in the laboratory and in the field before large-scale application to shorelines. Rigorous chemical analyses were needed to establish rates of biodegradation. Laboratory tests provided critical scientific information, but were considered inadequate for ensuring that bioremediation was applicable to the actual shorelines impacted by oil from the *Exxon Valdez* spill. Field testing was critical for establishing efficacy and safety;

(3) Bioremediation and natural oil biodegradation have limitations and are not effective in all environments. Bioremediation was shown to be effective in highly porous shorelines where nutrients and oxygenated seawater could reach the surface and sub-surface oil residue. However, it will be no more effective than natural biodegradation if oil is sequestered from the significant water flow needed to transport nutrients and oxygen;

(4) Bioremediation will not result in the complete removal of all of the oil;

(5) Naturally-occurring, hydrocarbon-degrading bacteria are widespread and introducing new bacteria is not necessary. Non-native bacteria that work well in the laboratory might not necessarily be useful for real-world application to an oil spill, their effectiveness would have to be scientifically demonstrated in the field, and would need to overcome government and public concerns about the introduction of non-indigenous microorganisms;

(6) Scaling-up is a critical factor that must be considered in a real-world application of bioremediation. Full-scale application of bioremediation required major logistical considerations and monitoring to ensure effectiveness. Practical logistical constraints generally dictated that fertilizers applied be slow-release or oleophilic;

(7) The decision to use bioremediation should be based on a net environmental benefit analysis. If residual oil poses no ecological risk, it should be left to undergo natural biodegradation;

(8) Bioremediation lessons learned from the *Exxon Vald*ez spill are applicable to other marine shorelines. Site-specific differences, however, will require additional considerations.

In contrast to the *Exxon Valdez* tanker surface spill, the more recent BP *Deepwater Horizon* spill was a leak from a well 1500 metres below the ocean surface that created both a deep-sea "plume" of oil and methane that moved in the deep water away from the wellhead and a surface water oil slick, more than 80 km from the nearest shore. Some oil did wash ashore, contaminating marshes and sandy beaches.

The chemical dispersant Corexit was added at the wellhead directly to the leaking oil as well as to surface slicks. One might consider the addition of dispersant in deep water as a form of bioremediation since it increased the surface area available for microbial attack. Hazen and co-authors [30] reported that there was rapid biodegradation of saturated hydrocarbons in the finely dispersed oil within the deep water even though temperatures were about 5°C. They reported that the psychrophilic bacterium *Oceanospirillales* was primarily responsible for hydrocarbon biodegradation. Redmond and Valentine [79] also reported that additional naturally occurring microbial populations responded to the presence of oil and were capable of rapid biodegradation of aromatic as well as aliphatic hydrocarbons. Valentine and co-authors [80] used circulation models to help explain the rapid biodegradation of alkanes, concluding that the oil droplets initially circulated around the wellhead where they were inoculated by adapted hydrocarbon degrading bacteria before advection to the Southwest by the prevailing currents. Oil that reached the marshes also was rapidly biodegraded [81].

In conclusion, when oil is highly dispersed in the water column and where microbial populations are well adapted to hydrocarbon exposure, such as in Gulf of Mexico waters, biodegradation of oil proceeds very rapidly. Bioremediation through fertilizer addition can be an effective means of speeding up rates of oil biodegradation in some situations, as evidenced by the *Exxon Valdez* spill, which remains the only case where large scale bioremediation has been used in the cleanup efforts. However, 100% removal of oil by biodegradation should not be expected — patches of highly weathered oil are likely to remain in some environments. Decisions whether or not to rely upon microbial oil biodegradation, including whether to apply bioremediation, should be driven by risk, and not just by the presence of detectable hydrocarbons. Risk-based corrective action (RBCA) has become an accepted approach to remediating contaminated sites [82]. In this approach the risks to human health and the environment are evaluated and corrective measures to reduce risk to an acceptable level are taken [83]. If the level of hydrocarbons detected poses no risk, then a remedial strategy is not indicated.

Response strategies for terrestrial oil spills

In total, more oil spills occur on land than on water due to thousands of kilometers of pipelines crossing producing/consuming countries and intensive transfers between pipelines and storage facilities, and rail and road tankers operating daily throughout the world. Most of these spills remain unreported to the public as they do not generate dramatic visual images that are associated with marine tanker or platform accidents [7]. As a consequence of less public concern for terrestrial spills, less emphasis on research and planning has been made compared to marine or coastal spillages. For example, clean-up endpoint evaluation criteria, sensitivity analysis and net environmental benefit concepts are still under-developed for terrestrial oil spills. Nevertheless, recent tendencies to estimate the economical value of healthy soil [84] and better understanding its vital importance for the survival of our planet [85] would increase public concern for soil and groundwater contamination.

Prevention of oil spillage on land

E.H. Owens [7] summarized potential advantages and disadvantages of a response to terrestrial and marine oil spills (Table 3). Terrestrial spills generally have a greater risk of directly impacting human lives and resources associated with social or economic activities. Therefore, most response strategies focus on prevention and, in case of accident, containment and control to minimize the spread of spilled material. Oil spill prevention measures for the Trans-Alaska Pipeline System were described [86], including route selection, design, construction, personnel training, operation and maintenance. Hughes and Stallwood [87] stated that, especially for fragile cold ecosystems, it is economically and environmentally preferable to prevent oil spills rather than undertake costly land remediation.

Prevention of oil penetration into groundwater/surface waters

An important response strategy for terrestrial spills is to prevent the spilled material reaching groundwater and surface waters. Current containment and protection methods are summarized in Table 4. Selecting the appropriate technique depends on amount and type of oil spilled, surface properties, and available response time. One operational objective could be to contain the spilled material to make recovery easier, for example, by damming to allow the use of skimmers [7].

Advanced clean-up methodologies and technologies

Even where appropriate spill response technologies have been deployed there will frequently be a requirement to treat significant quantities of contaminated soil and groundwater and a variety of physical, chemical and biological approaches may be applied singly or as a treatment train. Human health and/or environmental risk based criteria are widely applied in contaminated land remediation [88] to determine target treatment levels.

Morais and Delerue-Matos [89] critically reviewed the challenges concerning the life cycle assessment (LCA) application to land remediation services. They concluded that, in site remediation decision-making, LCA can help in choosing the best available technology to reduce the environmental burden of the remediation service or to improve the environmental performance of a given technology. However, this is a new approach with little legislative authority, and its application requires time, skill, and adds to the cost of a project. Also the standardisation and certification of remedial techniques has been discussed as a means of ensuring the quality of the ‘product’, cleaned soil [90]. Also, some initial work on eco-efficiency of remedial technologies has been done (Table 5) [91].

The most frequently used established technologies in the US are incineration, thermal desorption, solidification/stabilization and soil vapour extraction (SVE), and, for groundwater, pump-and-treat technologies [92]. Interestingly, SVE and thermal desorption were until recently classed as innovative technologies, but they have crossed the barrier to implementation and are now established.

Thermal treatment

The selection of the most appropriate thermal treatment technology will consider the nature of oil, soil type and heterogeneity and perhaps most importantly the scale of the area to be treated. Mobile thermal technologies exist and depending on the availability and proximity of fixed treatment units, it may be more cost-effective to take materials away from the spill location for treatment.

Incineration is the high-temperature thermal oxidation of contaminants to destruction. Incinerators come as a variety of technologies – rotary kiln, fluidised bed, infra-red [93]. A typical incinerator system consists of waste storage, preparation and feeding; combustion chamber(s); air pollution control; residue and ash handling; process monitoring. Rotary kilns are the most common incinerators for waste materials [94]. The rotary kiln is a cylindrical, refractory-lined reactor set at a slight angle (rake). As the kiln rotates, the waste moves through the reactor and is mixed by tumbling [95]. Incineration offers a very attractive advantage in that removal efficiencies of beyond 99 % have been reported. It can work on a very large range of soil types, and results in detoxification.

Most common incinerators used for contaminated soil are rotary kiln and fixed hearth, and the fluidised bed. Rotary kiln and fixed hearth are twin chamber processes. The primary chamber volatilises the organic components of the soil, and some of them oxidise to form carbon dioxide and water vapour at 650-1250°C. In the second chamber, high temperature oxidation (about 1100-1400°C) is used to completely convert the organics to carbon dioxide and water.

Fluidised bed incinerators, by contrast are single chamber systems containing fluidising sand and a headspace above the bed. Fluidisation with pressurised air creates high turbulence and enhances volatilisation and combustion of the organics in contaminated soil.

Most of the reported limitations of soil incineration are operational problems. For example, there are specific feed size and materials handling requirements that can impact on applicability or cost. Volatile metals can exit the incinerator with the flue gases, entailing additional gas treatment facilities. Sodium and potassium form ashes, which are aggressive to the brick lining. Above all, incineration is a costly, high-energy operation with poor public perception due to *de novo* synthesis of dioxins and furans. It also destroys the soil, so does not score highly as a sustainable technology.

Low temperature thermal desorption (LTTD) involves two processes: transfer of contaminants from the soil into the vapour phase (volatilisation) (about 120-600 °C); and higher temperature off-gas treatment (up to 1400 °C). It can be used for small-scale projects as it is very flexible in operation e.g. variable temperature, use of catalysts. It has a distinct advantage over incineration in that the soil is not destroyed. It may be more or less sterilised but there is a market for sterile topsoil. LTTD can remove petroleum hydrocarbons from all soil types.

The use of LTTD has advanced to the point where many US states have approved/permitted multiple LTTD units for petroleum-contaminated soil. The recent trend for LTTD is towards larger fixed facilities as opposed to mobile facilities. This trend is likely due to economies of scale, public acceptance issues, and site size restriction [96].

Major operational problem encountered in thermal desorption treatment of contaminated soil involves particulates. All LTTD systems require treatment of the off-gas to remove particulates and organic contaminants. Dust and soil organic matter affect the efficiency of capture and treatment of off-gas. Volatile metals such as mercury may also cause operational problems.

The energy efficiency and therefore economic performance of thermal desorption especially in wet soils may be improved by pre-treatment using microwave heating to remove moisture and a proportion of petroleum contamination [97]. Microwave energy has also been reported for rapid recovery of crude oil from soil. It was recently reported [98] that microwave heating enhanced by carbon fiber added as a microwave absorber was able to recover 94% of crude oil contaminant.

Stabilization/Solidification

Treatment agents or ‘binders’ can be used to prevent leaching of contamination to achieve stabilization or immobilize contamination by forming a solid mass, i.e. solidification. Typical binders include lime, cement and more recently fly ash [99]. Alternatives have been tested e.g.

polyacrylamide but this was not found be successful [100]. The technology may be applied *in-situ* by injecting binders into the contaminated zone or *ex-situ*. Physical treatment by solidification/stabilization may be particularly attractive in certain locations e.g. for spills where treated material can be reused on-site or in construction applications [101].

Significant reductions in total concentrations and leaching of petroleum hydrocarbons have been reported with the simultaneous improvement in soil strength due to binder addition [102]. This may be explained by a combination of volatilization and encapsulation within the treated matrix that reduces extractability of petroleum hydrocarbons.

Soil vapour extraction

A soil vapour extraction (SVE) approach is more effective for lighter oil fractions, particularly in warmer climates. It can be applied to volatile compounds with a Henry's law constant greater than 0.01 or a vapour pressure greater than 0.5 mm [103]. Most crude oils have a low rate of evaporation and result in low recoveries.

SVE removes volatile and semi-volatile contaminants from the unsaturated zone by applying a vacuum connected to a series of wells. Vacuum pumps or blowers induce a pressure gradient in the sub-surface, resulting in an airflow field about an extraction well [94]. These systems can be combined with groundwater pumping wells to remediate soil previously beneath the water table.

Gas- and vapour-phase contaminants are removed via advective airflow entering the extraction wells. High vapour pressure contaminants are removed first, and the soil progressively becomes enriched in less volatile compounds. While SVE does not remove heavy oil fractions from soil, it encourages aerobic biodegradation. An important limitation is the inability to treat soils of low porosity or in the saturated zone.

Pump-and-treat technologies

This widely used technology refers to extraction and *ex-situ* treatment of contaminated groundwater. Once treated, this may be returned to recharge the aquifer or disposed/further treated elsewhere. Where practicable, a key intervention at spill sites is to install skimmer pumps in groundwater wells to remove as much the recoverable free product as possible to minimise the on-going source of contamination. Recovery of heavy refined hydrocarbon fractions and crude oil is problematic due to low water solubility. Surfactants may be used to enhance recovery and reduce cost and time of remediation.

High costs and long time scales associated with pump-and-treat remediation favoured the use of natural attenuation processes in the sub-surface, especially biodegradation by naturally occurring microorganisms. However, Essaid and co-authors [104] highlighted findings from a survey of ten closed hydrocarbon contaminated sites in the US where the benzene concentrations were found to be greater after closure than during the period of monitored natural attenuation. Such uncertainties along with time and cost considerations have also favoured development of alternative approaches such as *in-situ* use of nano-scale zerovalent-iron or nano-sized oxides [105].

Bioremediation

Bioremediation, based on biological processes for the clean-up of contaminated land and groundwater, may improve the soil quality and appears more sustainable than other remedial technologies (e.g. incineration or solvent treatment). Several reviews (e.g. [106, 107]) described principles and main advantages of bioremediation approaches for organic pollutants. While natural attenuation requires only monitoring, implementation of accelerated biopile- or bioreactor-based processes may be directed to exploiting microbial technology and bioprocess engineering to enhance contaminant degradation [108]. Bioremediation technologies (Fig. 4) are divided broadly between *ex-situ* and *in-situ* methods. *Ex-situ* technologies involve the construction of windrows or biopiles, either on site or at a remote location. *In-situ* technologies are much less obtrusive, involve significantly fewer earthworks, but require longer treatment times and suffer from a lack of control compared to *ex-situ* technologies [84].

Composting uses windrows or biopiles constructed on lined areas to encourage biological degradation of oil contaminants. Aeration, leachate and runoff control are built into the system design. Blowers are used either to draw or to push air through the soil. Air movement is used to control temperature and oxygen concentration within the pile. Alternatively, solid-phase peroxide may be used as an oxygen source, thereby reducing the need for engineered air movement. Bulking agents such as wood chips are used to aid the air flow. Microbial inocula can be added, depending on whether or not an indigenous hydrocarbon-oxidizing population can be stimulated [109]. The soil water content is monitored and adjusted with supplemental inorganic or organic nutrients. However, nutrient amendment with elevated nitrogen concentration has detrimental effects on hydrocarbon degrading fungal populations due to the ammonia gas production by nitrification [110].

Landfarming is a biological treatment technology in which oily wastes are applied to soil surfaces, which is periodically tilled and watered to enhance biodegradation rates. While being widely practiced in the oil industry, landfarming of refinery and wellhead oily sludges is not considered environmentally acceptable in many cases because it is unacceptable to deliberately contaminate large land areas and because of high volatile hydrocarbon emission causes odor problems [108]; in some cases well managed landfarming operations are appropriate and effective for treating crude oil contaminated soils.

A potential problem in solid-phase soil treatment is the residual heavy oil fractions strongly adsorbed to the soil matter and hardly degraded by soil microorganisms. The addition of (bio)surfactants can increase the release and subsequent biodegradation rates [111]. Biosurfactants produced by hydrocarbon-oxidizing bacteria, less toxic and more biodegradable compared to synthetic surfactants, are promising bioremediation agents [112-114].

Performing bioremediation in a prefabricated bioreactor gives the ultimate in flexibility with the greatest degree of process control. Particularly, bioreactor technologies allow precise control and management of biodegradation parameters such as temperature, pH, oxygen, nutrient and water contents, homogenous distribution of contaminated material and biomass in the reactor volume, which leads to increased mass transfer and reaction rates [108]. However, bioreactor processes are currently used for petrochemical and refinery wastes rather than crude oil-contaminated soil due to high operational costs. A pilot-scale bioreactor was designed to treat crude oil-contaminated soil in a slurry phase followed by the soil after treatment in landfarming plots [115]. For contaminated soils and sediments a bioreactor-based treatment train may use: biofilms or suspended microorganisms; native microbial populations from the material being treated; selected laboratory cultures; specific genetically engineered microorganisms (GEMs). The latter can be used in contained bioreactor systems without risks associated with GEM introduction into natural ecosystems [116].

In-situ bioremediation comprises various techniques which minimize intrusion and, therefore operational costs. Most *in-situ* processes involve the stimulation of indigenous microbial populations (biostimulation) so that they become metabolically active and degrade the contaminant(s) of concern.

Problems encountered during *in-situ* stimulation of microbial populations include the plugging of wells and sub-surface formations by the biomass generated through microbial growth on hydrocarbons, difficulties in supplying sufficient oxygen to the sub-surface, and the inability to move nutrients and electron acceptors to all regions of heterogeneous sub-surface environments. Also, it is rarely possible to remove all free product, so reservoirs of slowly released contamination may be present for many years.

Almost certainly the availability of molecular oxygen is the greatest problem facing *in-situ* bioremediation for oil hydrocarbons that are biodegraded aerobically. This problem is especially profound in waterlogged soils, as circulation of air is hindered. For *in-situ* bioremediation of surface soil, oxygen availability is best assured by providing adequate drainage. Air-filled pores in soil facilitate diffusion of oxygen to hydrocarbon-oxidizing microorganisms, while in waterlogged soil, oxygen diffusion is extremely slow and cannot satisfy the demand of biodegradation processes. Plugging and roto-tilling have been used to turn the soil and assure its maximal access to atmospheric oxygen. Adding dilute solutions of hydrogen peroxide in appropriate and stabilized formulations can also be used to supply oxygen for hydrocarbon biodegradation [117].

Air sparging is an *in-situ* technology which can be utilized either to remove volatile compounds from the sub-surface or to induce microbially mediated treatment in water-saturated soil [118]. During air sparging, air is injected into the saturated zone, usually below the target clean-up zone. Volatile compounds dissolved in groundwater and sorbed on soil particles will partition into the air phase and be transported to the vadose zone. The volatilized compounds can then be collected from the vadose zone by a soil vapour extraction system, or degraded by indigenous microbes.

Bioventing is becoming an attractive option for promoting *in-situ* biodegradation of readily biodegradable pollutants like petroleum hydrocarbons [119]. Bioventing is a process which employs enhanced oxygenation in the vadose zone to accelerate contaminant biodegradation. This technology is also highly effective when paired with bioremediation in the saturated zone (bio-sparging). When properly implemented, bioventing often results in faster, more cost-effective remediation. Details of bioremediation technologies and their design can be found in [120].

A plethora of genome-wide (–omics) technologies, biosensors, and community profiling techniques, so-called ‘ecogenomics’, are available to improve bioremediation in the field [84].

Ecogenomics approaches could be used to characterize contaminated sites and monitor the bioremediation process. Metagenomics or metatranscriptomics can identify microorganisms and catabolic genes present in contaminated soil and, when amended with software tools, can predict the final levels of pollutants after bioremediation treatments. There is an urgent need to equip bioremediation practitioners with a suite of –omics techniques to demonstrate the genuine scientific basis that underpins the process, and to improve its predictability [121].

Concluding remarks

Since oil exploration is being driven into deeper waters and more remote, fragile places like the Arctic, then the risks of future accidents become much higher, so safety and accident prevention have to be strategic priorities for the oil industry. Greater international cooperation in contingency planning and spill response would probably lead to higher safety standards and fewer accidents. Among clean-up technologies available for marine and terrestrial oil spills, bioremediation methods appear more sustainable and cost-effective and their successful penetration into the remedial technologies market depends greatly on harmonization of environment legislation and the application of modern laboratory techniques, e.g. ecogenomics to remove field-scale uncertainties. Nevertheless, prevention is far less expensive than cure, and oil spill prevention should continue to be the focus for the industry.

Acknowledgements
This work was partially funded by the Perm Ministry of Education grant for International Research Groups and the Russian Science Foundation grant 14-14-00643.

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Table 1. Comparison between marine and terrestrial oil spills [7]

Marine	**Terrestrial**
Oil behavior	
Oil remains in motion: sometime difficult to locate. Moved by winds and/or currents. Degree of unpredictability and uncertainty. Generally spreads to form a very thin surface layer. Weathering and emulsification are rapid.	Generally slow moving or static. Collects in depressions or water courses. Easy to define location and amount of surface oil. Only light oils spread to form a thin layer; often considerable pooling of oil. Weathering slows considerably after ~24 h.
Resources at risk	
Some are mobile – fish, birds, boats. Few resources at risk on the actual water surface. Vulnerability is uncertain.	Some mobile resources – birds; often many static resources – buildings, vegetation, crops. Except in remote areas, usually many more resources at risk. Risks easy to identify.
Response operations	
Water based. Weather dependent – fog, winds, waves, currents, etc. Predominantly mechanical response (booms and skimmers) with potential for burning or dispersant. Often requires considerable support.	Land based. Usually not weather dependent. Predominantly manual response in most cases. Usually remove a higher percentage of the oil as weathering slowly and cleanup standards are stricter.

Table 2. Top ten blowout incidents world-wide

Well	**Location**	**Date**	**Tons**
Deepwater Horizon	Macondo Prospect, Gulf of Mexico, US	Apr. 2010	686,000[1]
Ixtoc 1	Bahia de Campeche, Mexico	Jun. 1979	471,430
Pemex Abkatun 91	Bahia de Campeche, Mexico	Oct. 1986	35,286
Phillips Ekofisk Bravo	North Sea, Norway	Apr. 1977	28,912
Nigerian National Funiwa 5	Forcados, Nigeria	Jan. 1980	28,571
Aramco Hasbah 6	Gulf of Arabia, KSA	Oct. 1980	15,000
Iran Marine International	Off Laban Island, Iran	Dec. 1971	14,286
Union Alpha Well 21	Santa Barbara, CA, US	Jan. 1969	14,286
Chevron Main Pass 41-C	Gulf of Mexico, Louisiana, US	Mar. 1970	9,286
Pemex Yum 2/Zapoteka	Bahia de Campeche, Mexico	Oct. 1987	8,378

[1] Based on 4.9 million barrels (from [122]). All other data from [123].

Table 3. Potential advantages and disadvantages of spills on land compared to those on water (generated from [7])

Advantages	**Disadvantages**
Usually the impacted area is relatively small.	Slower weathering and natural attenuation.
Greater potential for predicting the movement and effects of a spill.	Greater potential for impacting human-use activities and resources.
Greater operational opportunities and flexibility, and greater recovery potential.	Potential for more strict cleanup standards and endpoints.

Table 4. Containment and control techniques used for terrestrial oil spills

Technique	Description	Limitations	Potential environmental effects
Containment/ diversion berms	Low barriers constructed with locally available materials (e.g., soil, gravel, sandbags, etc.) are used to contain or direct surface oil flow	Limited accessibility Steep terrain Implementation time Highly permeable soils and low-viscosity oils	Environmental damage inflicted by excavation of berm materials
Trenches	Dug by machinery to contain and collect oil for recovery or to intercept surface/subsurface oil flow	Limited accessibility Implementation time Highly permeable soils and low-viscosity oils High water table	Environmental damage inflicted by trench excavation
Sorbent barriers	Low elevation sorbent barriers are used on relatively flat or low-slope terrain to contain or immobilize minor oil flows and recover oil; or to limit penetration into permeable soils	Implementation time Steep slopes	Winds may blow sorbents into the surrounding environment
Culvert/drain blocking	Sandbags, boards, mats, earthen or other materials are used to block culverts or to prevent oil spilled on roadways and paved areas	Limited accessibility Implementation time Storage area behind culvert Flowing water Culvert size	
Slurry walls	A vertically excavated trench is filled with slurry to contain or divert contaminated groundwater, or to provide a barrier for the groundwater treatment system	Wall may degrade over time Specific contaminants may degrade wall components	Environmental damage inflicted by trench excavation
Viscous liquid barriers	When injected in the subsurface, viscous liquids form inert impermeable barriers that contain or isolate contaminants		

Table 5. Eco-efficiency of some selected contaminated land remediation technologies (modified from [91]).

Remediation method	**Positive factors**	**Negative factors**
Reactive barrier	Generally no need for removal of the barrier	Long-term operating costs, suitable only for some contaminants
Soil stabilisation, isolation	No need for soil removal; quick; can be economical	No removal of contaminants from environment; can be energy-intensive
Soil vapour extraction (SVE)	Generally cost-effective; low uncertainties in risk reduction	Suitable only for volatile contaminants; exhaust air needs to be treated
Incineration (mobile)	Effective contaminant removal	Flue gas treatment needed; energy-intensive; often needs fuel
Composting	Low cost; treated soil may be used for landscaping; no emissions requiring treatment	Suitable only for some organic contaminants; can be long duration; depends on contaminant concentrations
Landfill	Effective control of risks; soil can be used in daily cover	Not suitable for re-use; becoming more expensive; not efficient use of landfill sites

List of figures

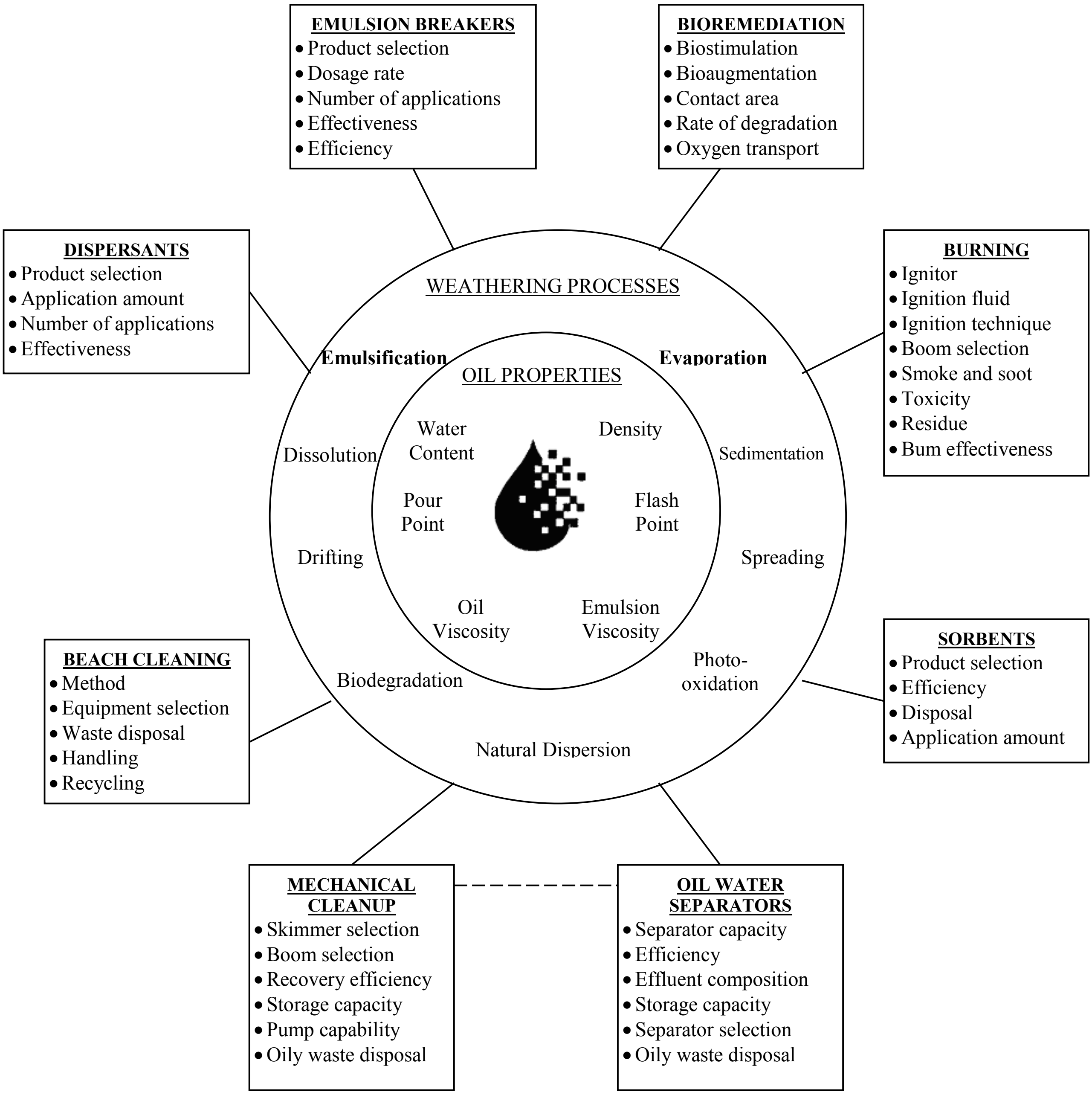

EMULSION BREAKERS
• Product selection
• Dosage rate
• Number of applications
• Effectiveness
• Efficiency
BIOREMEDIATION
• Biostimulation
• Bioaugmentation
• Contact area
• Rate of degradation
• Oxygen transport
DISPERSANTS
• Product selection
• Application amount
• Number of applications
• Effectiveness
BURNING
• Ignitor
• Ignition fluid
• Ignition technique
• Boom selection
• Smoke and soot
• Toxicity
• Residue
• Bum effectiveness
WEATHERING PROCESSES
Emulsification
Evaporation
OIL PROPERTIES
Dissolution
Water Content
Density
Sedimentation
Pour Point
Flash Point
Drifting
Spreading
Oil Viscosity
Emulsion Viscosity
Biodegradation
Photo-oxidation
Natural Dispersion
BEACH CLEANING
• Method
• Equipment selection
• Waste disposal
• Handling
• Recycling
SORBENTS
• Product selection
• Efficiency
• Disposal
• Application amount
MECHANICAL CLEANUP
• Skimmer selection
• Boom selection
• Recovery efficiency
• Storage capacity
• Pump capability
• Oily waste disposal
OIL WATER SEPARATORS
• Separator capacity
• Efficiency
• Effluent composition
• Storage capacity
• Separator selection
• Oily waste disposal

Figure 1

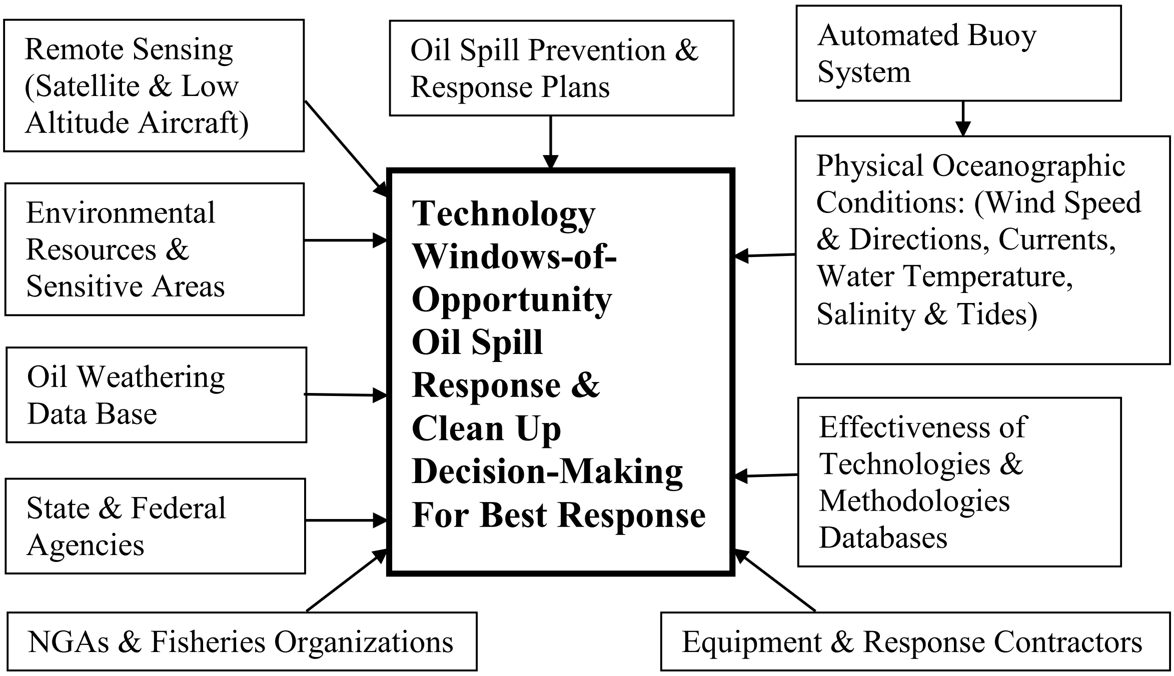
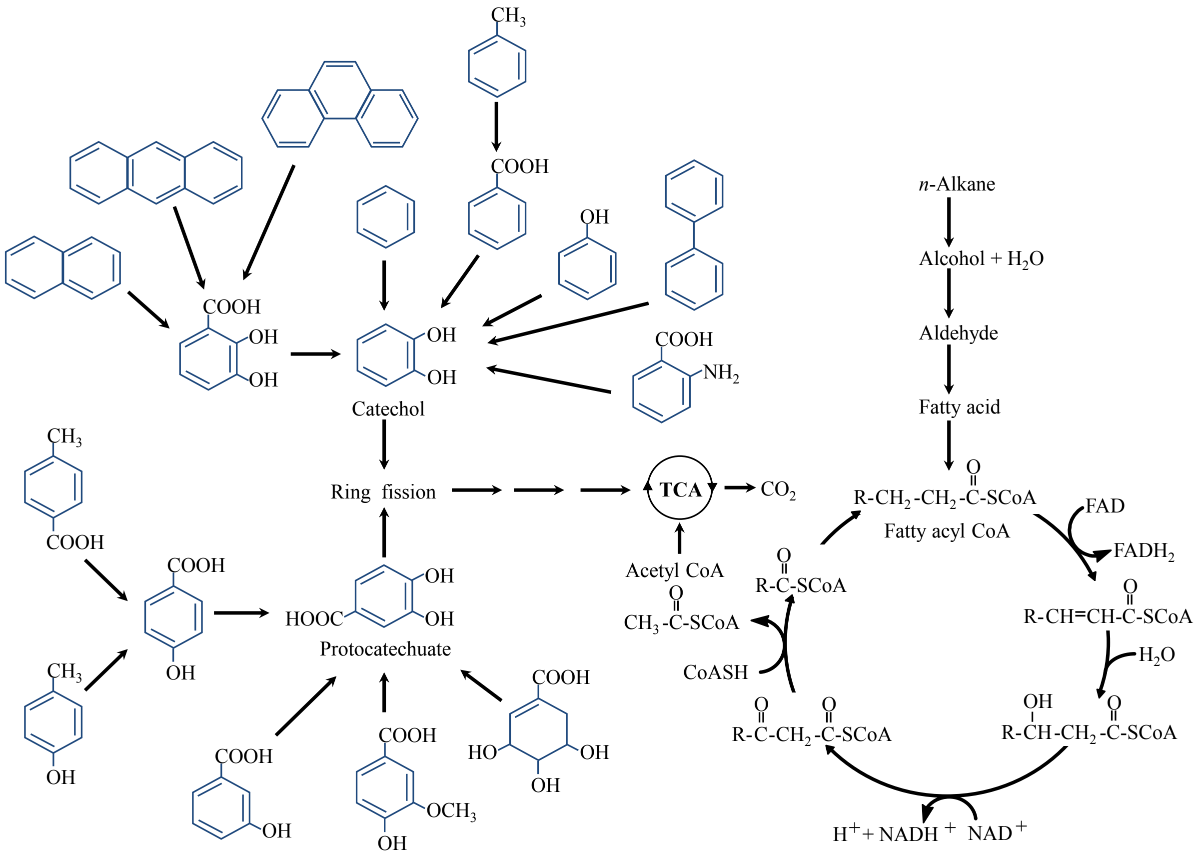

Remote Sensing (Satellite & Low Altitude Aircraft)
Oil Spill Prevention & Response Plans
Automated Buoy System
Environmental Resources & Sensitive Areas
Technology Windows-of-Opportunity Oil Spill Response & Clean Up Decision-Making For Best Response
Physical Oceanographic Conditions: (Wind Speed & Directions, Currents, Water Temperature, Salinity & Tides)
Oil Weathering Data Base
Effectiveness of Technologies & Methodologies Databases
State & Federal Agencies
NGAs & Fisheries Organizations
Equipment & Response Contractors

Figure 2



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Alcohol + H2O
Aldehyde
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Ring fission
TCA
CO2
R-CH2-CH2-C-SCoA
Fatty acyl CoA
FAD
FADH2
CH3
COOH
COOH
OH
OH
HOOC
OH
Protocatechuate
Acetyl CoA
CH3-C-SCoA
R-C-SCoA
R-CH=CH-C-SCoA
H2O
CoASH
CH3
OH
COOH
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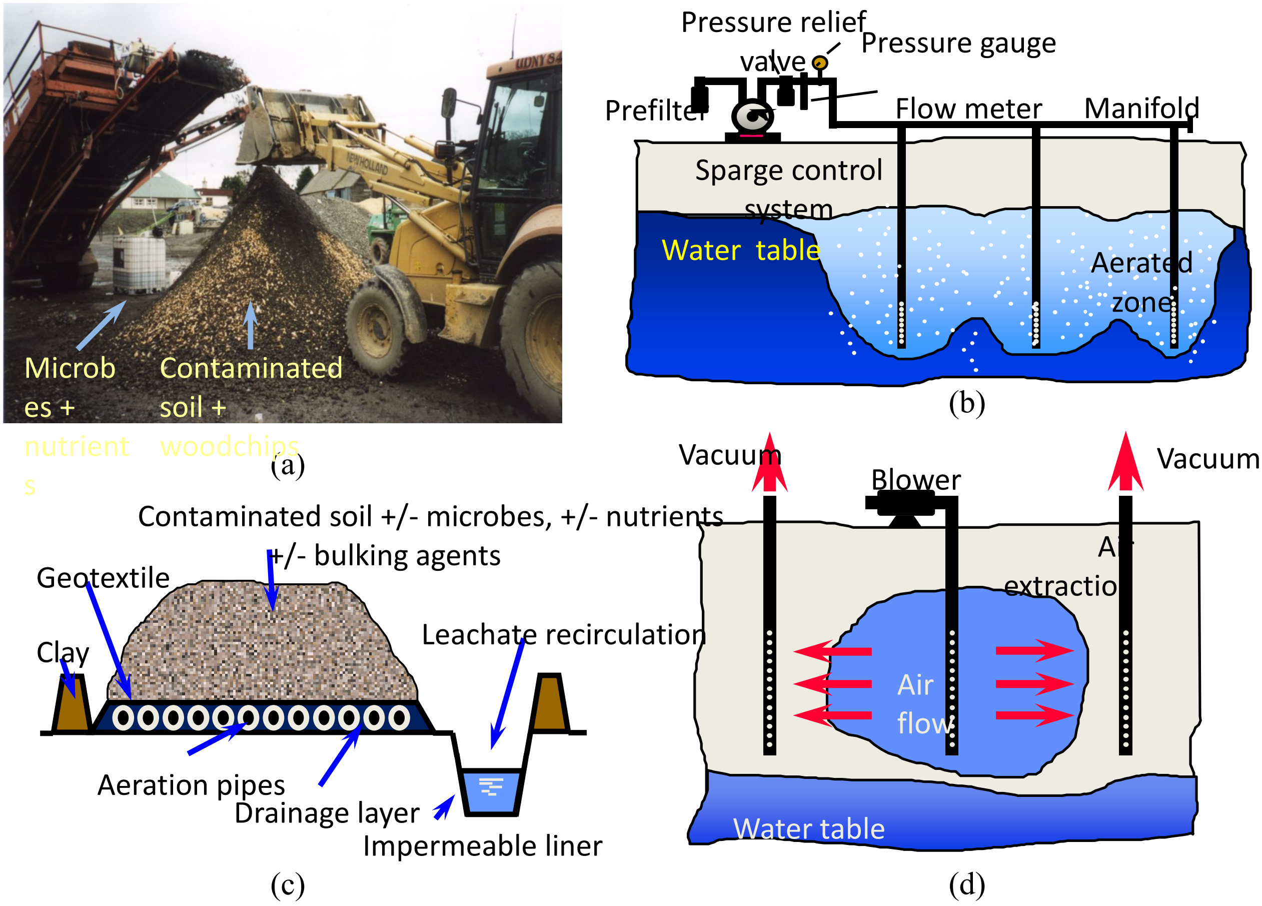
NAD+

Figure 3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Prefilter
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Manifold
Sparge control
system
Water table
Aerated
zone
(b)
Contaminated soil +/- microbes, +/- nutrients
+/- bulking agents
Geotextile
Clay
Leachate recirculation
Aeration pipes
Drainage layer
Impermeable liner
(c)
Vacuum
Blower
Vacuum
Air
extractio
Air
flow
Water table
(d)

Figure 4